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Preparation and Spectral Properties of Oxochromium(v) Complexes.

Orville Vernon Ziebarth

Louisiana State University and Agricultural & Mechanical College

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CHROMIUM(V) COMPLEXES.

The Louisiana State University and Agricultural
and Mechanical College, Ph.D., 1970
Chemistry, inorganic

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PREPARATION AND SPECTRAL PROPERTIES OF OXOCHROMIUM(V)
COMPLEXES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by
Orville V. Ziebarth
B.S., St. Cloud State College, 1958
M.S., Iowa State University, 1962
January 1970

TO MY WIFE, RENEE

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ABSTRACT

The purpose of this study was to better characterize the existing oxochlorochromium(V) complexes, prepare some new oxochromium(V) complexes, characterize the compounds by available methods, and to make comparisons with VO^{2+} and MoO^{3+} species both of which exhibit many and a variety of complexes. The preparative and other studies of CrO^{3+} compounds recorded in the literature are very few and generally quite incomplete. A complete study was undertaken of some of the existing chloro-species as well as some new chloro-species prepared here for the first time with other cations.

Two types of oxochlorochromium(V) complexes have been prepared, namely RCrOCl_4 and R_2CrOCl_5 , and since both are prepared by the same procedure it appears that the size of the cation involved determines which of the two complexes will be obtained in a given preparation. The largest cation that is known to form the R_2CrOCl_5 is the Cs^+ ($r = 1.67\text{\AA}$) whereas the smallest cation that is known to form the RCrOCl_4 species is the Me_4N^+ ($r = 3.4\text{\AA}$).

Spectra of these unstable complex species were taken in the solid state at room temperature and at 77°K and at room temperature in various solvents. From other physical-chemical data obtained in this investigation, such as conductance data, magnetic susceptibilities, ESR spectra, infrared spectra along with electronic spectral data, the observed electronic and vibronic

bands are now assigned more completely and are on a much firmer empirical basis. For the oxochlorochromium(V) compounds the following empirical energy assignments are proposed to account for the observed electronic transitions:

$(d_{xz}, d_{yz}) \leftarrow d_{xy}$	12.5kK
$d_{x^2-y^2} \leftarrow d_{xy}$	18.0kK
$d_{xy} \leftarrow \pi_{Cl}$	22.5kK
$d_{z^2} \leftarrow d_{xy}$	25-30kK

A new fluoro-complex, $(Et_4N)_2CrOF_5$, was isolated by a completely new method and characterized in the usual way. The electronic transitions observed for this complex are assigned in a manner consistent with those of the oxochloro-complexes; namely, the corresponding transitions are assigned to the bands at 8.3, 22.33, 14.87, and 25-31kK, respectively.

A new series of complexes of the general formula, $Cs_2CrO(AB)Cl_3$ where AB represents a hydroxy acid (tartaric acid, hydroxy malonic acid, or malic acid), have been prepared. More specifically these new complexes are $Cs_2CrO(OOCCHOHCHOHCOO)Cl_3$, $Cs_2CrO(OOCCH_2CHOHCOO)Cl_3$, and $Cs_2CrO(OOCCH_2CH_2COO)Cl_3$. These represent the first new complexes of CrO^{3+} to be isolated that have ligands other than Cl^- and F^- . Although the magnetic moment data for these complexes are in the range expected for a Cr(IV) complex, all other accumulated data (method of preparation, elemental analyses, ESR, IR and electronic spectra) point

firmly to Cr(V) complexes. The observed electronic spectral bands are assigned assuming that these compounds are d^1 species. The proposed assignments for the hydroxy acid complexes fit into the scheme proposed here for the chloro- and fluoro-complexes of oxochromium(V).

GENERAL INTRODUCTION

Numerous papers have appeared in the literature in recent years which involve the preparation and properties of complexes containing oxocations of transition metals. A particular oxocation system which has received considerable attention in this laboratory and others is the vanadyl species, VO^{2+} . This species is of special interest because the ground state configuration of the tetravalent vanadium is $\text{Ar}(3d^1)$ and hence it should be a simple and straightforward system for observation and interpretation of spectra. Likewise its similarities to the $\text{Cu}^{2+} - d^9$ system via the hole formalism is an additional bonus. There are numerous other oxocation systems which have similar structures to the vanadyl species. Though most of these are not as stable as the vanadyl species, and hence have not received as much attention, they lend themselves to interesting comparisons with the vanadyl system. One such system is the oxochromium(V) species which is the topic of concern in this dissertation.

The first oxochromium(V) compounds, reported in the literature by Weinland and Fiederer^{1,2,3}, were of the type RHCrOCl_4 and M_2CrOCl_5 , where RH = pyridinium or quinolinium and $\text{M} = \text{K}^+$, Rb^+ , Cs^+ , or NH_4^+ . These compounds were prepared by reducing CrO_3 in

¹Weinland, R.F., and Fiederer, M., Ber., 38, 3784 (1905).

²Weinland, R.F., and Fiederer, M., Ber., 39, 4042 (1906).

³Weinland, R.F., and Fiederer, M., Ber., 40, 2090 (1907).

glacial acetic acid with hydrogen chloride and adding to this another solution of acetic acid saturated with hydrogen chloride and containing the appropriate chloride salt.

Sharp and Woolf⁴ prepared the fluoro complex of oxochromium(V) by fluorinating $K_2Cr_2O_7$ or $Ag_2Cr_2O_7$ with BrF_3 and they obtained $KCrOF_4$ and $AgCrOF_4$. $KCrOF_4$ was prepared more recently by Clark and Sadana⁵, who employed other halogen fluorides such as ClF_3 and BrF_5 . Other chromium(V) compounds containing fluoride that have been prepared are CrF_5 ⁶ and $CrOF_3 \cdot 0.25BrF_3$ ⁷.

Krauss, Manfred, and Muenster⁸ studied the reduction of CrO_3 with chloride ions by optical methods. The optical investigation of the reduction of chromium trioxide with hydrogen chloride in acetic acid demonstrated a course of reaction via CrO_2Cl_2 to oxochlorochromate(V) anions. $[(CrOCl_4)]^- / [(CrOCl_5)]^{2-}$, and finally by a photochemical reaction to $[Cr(H_2O)Cl_5]^{2-}$. In their studies they produced a series of chloro-complexes of the type $RHCrOCl_4$ (R = univalent organic base), $R'H_2CrOCl_5$ (R' = bivalent organic base) and $RAcCrOCl_4$ (RAc = N-acetyl pyridinium ion or N-acetyl-quinolinium ion). They also prepared $CrOCl_3$ in crystalline form.

⁴Sharpe, A.G., and Woolf, A.A., J. Chem. Soc., 798 (1951).

⁵Clark, H.C., and Sadana, Y.N., Can. J. Chem., 42, 702 (1964).

⁶Glemser, H.R., and Hellberg, K.H., Angew. Chem., 2, 266 (1963).

⁷Clark, H.C., and Sadana, Y.N., Can. J. Chem., 42, 50 (1964).

⁸Krauss, H.L., Leder, M., and Muenster, G., Ber., 96, 3008 (1963).

by treating CrO_3 or CrO_2Cl_2 with SOCl_2 or SO_2Cl_2 ⁹; and a later method involved the use of BCl_3 with CrO_2Cl_2 ¹⁰.

Alkali and alkaline earth chromates(V)^{11,12} have been prepared and characterized^{13,14}. They are black or blue-black solids which are very hygroscopic and readily hydrolyze with disproportionation to chromium(III) and chromium(VI). Alkaline perchromates with the empirical formulas K_3CrO_8 , Na_3CrO_8 , $(\text{NH}_4)_3\text{CrO}_8$ and KMgCrO_8 have also been prepared^{15,16,17,18}. X-ray investigations^{19,20} of the crystal structure of perchromates have shown that the chromium

⁹Krauss, H.L., and Muenster, G., Z. Naturforsch., 17B, 344 (1962).

¹⁰Johannesen, R.B., and Krauss, H.L., Ber., 97, 2094 (1964).

¹¹Scholder, R., and Schwarz, H., Z. Anorg. Chem., 326, 11 (1963).

¹²Scholder, R., Schwochow, F., and Schwarz, H., Z. Anorg. Allg. Chem., 363, 10 (1968).

¹³Scholder, R., Angew. Chem., 66, 461 (1954).

¹⁴Bailey, N., and Symons, M.C.R., J. Chem. Soc., 203 (1957).

¹⁵Riesenfeld, E.H., Wohlers, H.E., and Kutsch, W.A., Ber., 38, 1885 (1905).

¹⁶Martinez, J.B., Anales Real Soc. Espan. Fis. Quim., 45B, 697 (1953).

¹⁷Martinez, J.B., Rios, B.R., and Brito, F., Anales Real Soc. Espan. Fis. Quim., 49B, 681 (1953).

¹⁸Rios, B.R., and Trujillo, P.G., An. Quim., 64, 55 (1968).

¹⁹Wilson, I.A., Arkiv. Kemi Mineral Geol., 15B, No.5 (1942).

²⁰Stomberg, R., and Brosset, C., Acta Chem. Scand., 14, 441 (1960).

atom is surrounded by four peroxide ions in an eight-coordinated dodecahedral configuration, and magnetic susceptibility^{21,22,23} measurements indicate the chromium is in a positive five state. The x-ray studies indicated that there are two sets of non-equivalent Cr-O bonds and the ESR results showed that the shorter Cr-O bonds are more covalent than the longer ones^{24,25}.

A topic of much concern in the literature has been the theoretical model proposed by Ballhausen and Gray²⁶ to account for the near-infrared, visible, and ultraviolet spectral bands of the vanadyl species in various types of chemical environments. Of particular interest in this study is the adoption of the Ballhausen and Gray model by Gray and Hare²⁷ to explain the near-infrared, visible, and ultraviolet absorption bands of $(\text{NH}_4)_2\text{CrOCl}_5$.

Gray and Hare assumed CrOCl_5^{2-} to have a tetragonal structure (C_{4v} symmetry) with a short Cr-O bond analogous to the structure of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ which is known from X-ray analysis. The coordinate system used was such that the oxo-group lies on the positive z-axis and the chloro-groups fall directly on the remaining Cartesian axes. A simple crystal field treatment predicts the splitting of the

²¹Tjabbes, B.T., Z. Anorg. Allgem. Chem., 210, 385 (1933).

²²Klemm, W., and Werth, H., Z. Anorg. Allgem. Chem., 216, 127 (1933).

²³Rios, B.R., and Hoarau, J., Compt. rend., 241, 1299 (1955).

²⁴McGarvey, B.R., J. Chem. Phys., 37, 2001 (1962).

²⁵Swalen, J.D., and Ibers, J.A., J. Chem. Phys., 37, 17 (1962).

²⁶Ballhausen, C.J., and Gray, H.B., Inorg. Chem., 1, 111 (1962).

²⁷Gray, H.B., and Hare, C.R., Inorg. Chem., 1, 363 (1962).

d orbitals into four energy levels, one of which is two-fold degenerate. Figure 1, taken from the Ballhausen and Gray paper, shows the removal of degeneracy as the symmetry of the ligand field becomes octahedral (O_h symmetry) and then tetragonal (C_{4v} symmetry). For each level the figure indicates the appropriate d orbital, the group theoretical symmetry designation of each orbital, and the energy as a function of Ds , Dt , and Dq . Dq is the crystal field splitting parameter which is a measure of the d level separation in an octahedral field while Ds and Dt are analogous parameters which specify the degree of tetragonality present in the field. From the simple diagram three d-d transitions are predicted: $(d_{xz}, d_{yz}) \leftarrow d_{xy}$ (energy = $3Ds + 5Dt$), $d_{x^2-y^2} \leftarrow d_{xy}$ (energy = $10Dq$) and $d_{z^2} \leftarrow d_{xy}$ (energy = $10Dq - 4Ds - 5Dt$). If all three transitions can be assigned, it is then possible to calculate Ds , Dt , and Dq .

The Gray-Hare molecular orbital diagram for $CrOCl_5^{2-}$ is shown in Figure 2. Oxygen pi orbitals are used in the energy level scheme but metal-chlorine pi bonding is neglected. By dropping in the 17 valence electrons (10 from 5 chlorines, 6 from oxygen, and 1 from the metal) one obtains the ground state configuration, 2B_2 , as $[(Ia_1^b)^2(IIa_1^b)^2(b_1^b)^2(e_\sigma^b)^4(IIIa_1^b)(e_\pi^b)^4(b_2)]$. The reflectance spectrum data observed for the compound, $(NH_4)_2CrOCl_5$, is tabulated in Table 1, which includes the Gray-Hare assignments and the configuration of the excited state for each assignment. Bonding sigma orbitals are designated as IC (inner core) and they

Figure 1. Energy Levels in Crystalline Fields of O_h and Compressed C_{4v} Symmetry, with $(-3D_s + 5D_t) > 0$.

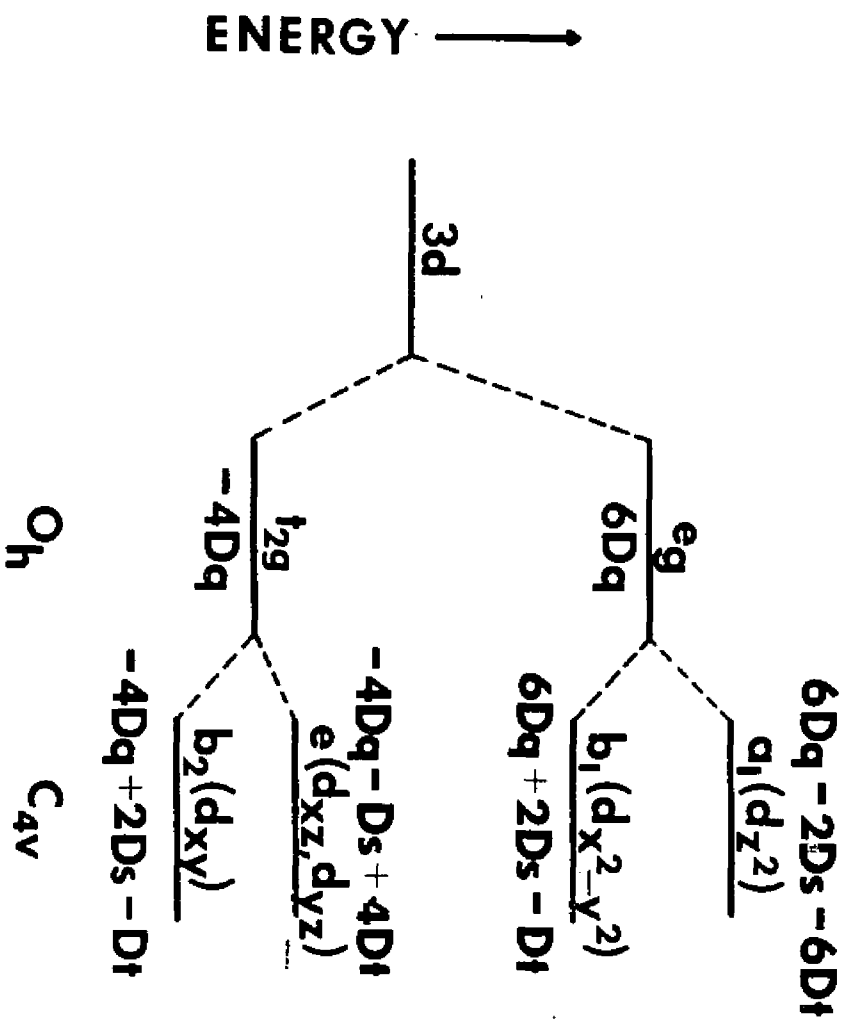


Figure 2. Molecular Orbital Diagram Proposed for $[\text{CrOCl}_5]^{2-}$ by Gray and Hare (ref.27).

CHROMIUM
ORBITALS

M.O. LEVELS

OXYGEN &
CHLORINE
ORBITALS

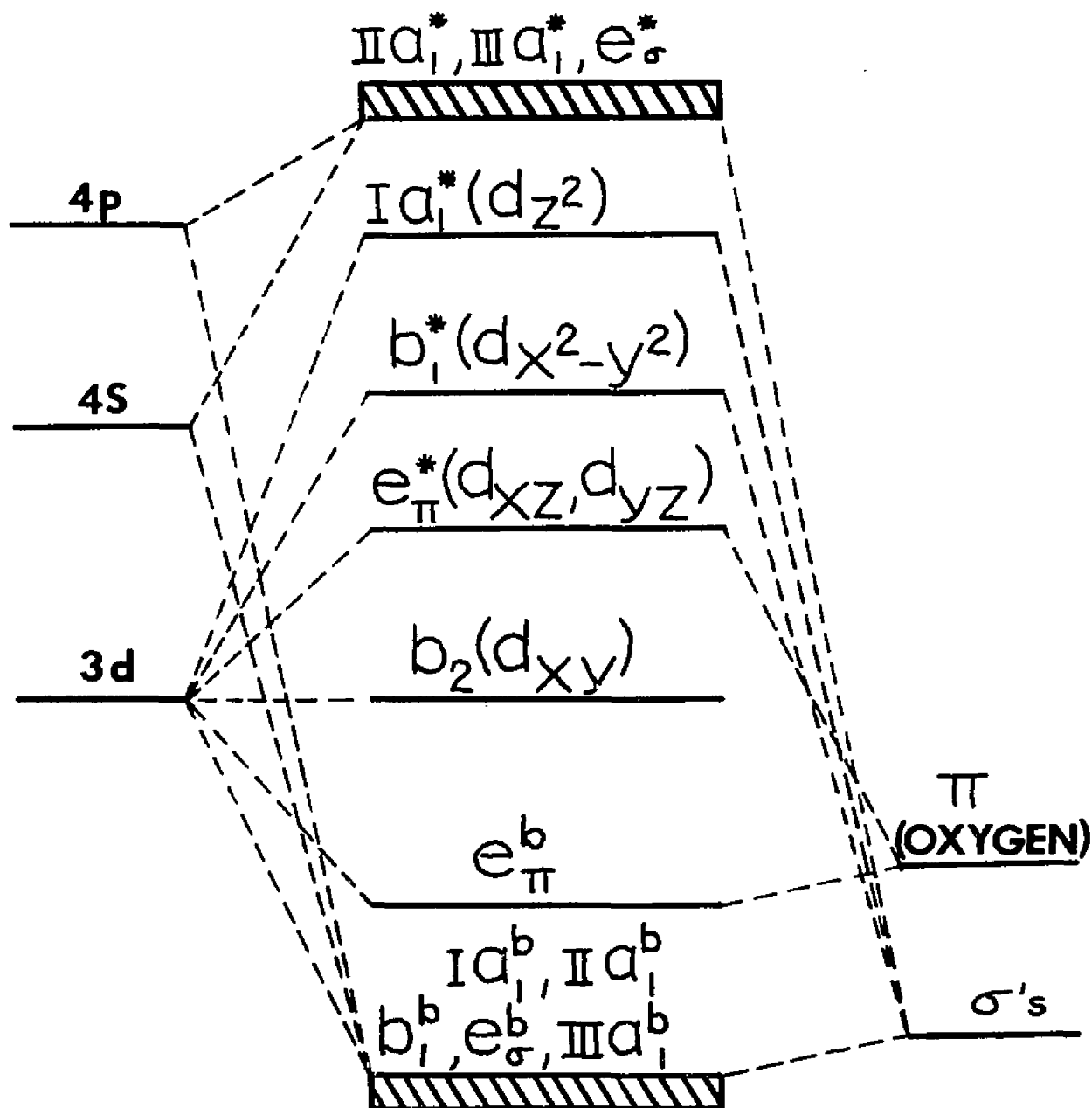


TABLE I

REFLECTANCE SPECTRUM DATA FOR $(\text{NH}_4)_2\text{CrOCl}_5$. ASSIGNMENTS
 ACCORDING TO GRAY AND HARE.²⁷

Frequency ^a	Transition	Excited State ^b
12.90	${}^2\text{E(I)} \leftarrow {}^2\text{B}_2$	$(\text{IC})^{12}(\text{e}_{\pi}^b)^4(\text{e}_{\pi}^{*})$
23.50	${}^2\text{B}_1 \leftarrow {}^2\text{B}_2$	$(\text{IC})^{12}(\text{e}_{\pi}^b)^4(\text{b}_1^{*})$
40.00 ^c	${}^2\text{E(II)} \leftarrow {}^2\text{B}_2$	$(\text{IC})^{12}(\text{e}_{\pi}^b)^3(\text{b}_2)^2$
44.40 ^d	${}^2\text{B}_2(\text{I}) \leftarrow {}^2\text{B}_2$	$(\text{IC})^{12}(\text{e}_{\pi}^b)^3(\text{b}_2)(\text{e}_{\pi}^{*})$

^aFrequencies are given in kiloKaysers (kK), $1\text{kK} = 1000\text{ cm}^{-1}$

^bThe ground state in each case is $(\text{IC})^{12}(\text{e}_{\pi}^b)^4(\text{b}_2)$.

^cShoulder

^dCalculated value (not observed experimentally).

are assumed to be unimportant for transitions in this spectral range. The third d-d transition is not observed and is assumed to be hidden under the first charge transfer band. No attempt was made by Gray and Hare to record aqueous solution spectra of $(\text{NH}_4)_2\text{CrOCl}_5$, since decomposition appears to take place very rapidly even in 10M HCl.

Hare, Bernal, and Gray²⁸ reported ESR and magnetic susceptibility measurements of the chromyl ion. The ESR spectrum of a solid sample of $\text{Rb}_2\text{CrOCl}_5$ showed a single broad resonance line centered at $g = 1.986$. The g value indicates an orbitally non-degenerate ground state and differs from 2.0023 (the free electron value) due to the mixing of the ground state and excited states via a spin-orbit coupling mechanism. From expressions for the g values for d^1 transition metal oxocations in C_{4v} symmetry²⁶ they were able to calculate $g_{||}$ and g_{\perp} on the assumption that they had correctly assigned the first two ligand field electronic transitions. The g value expressions for a d^1 transition metal oxocation in a C_{4v} ligand field are²⁶

$$g_{\perp} = 2.0023 \left(1 - \frac{\xi}{\Delta E(^2E(T) - ^2B_2)} \right) \quad \dots 1$$

$$g_{||} = 2.0023 \left(1 - \frac{4\xi}{\Delta E(^2B_1 - ^2B_2)} \right) \quad \dots 2$$

$$\langle g \rangle^2 = 1/3(2g_{\perp}^2 + g_{||}^2) \quad \dots 3$$

²⁸Hare, C.R., Bernal, I., and Gray, H.B., Inorg. Chem., 1, 831 (1962).

In these equations ξ is the spin-orbit coupling constant for Cr^{5+} in CrO^{3+} and the ΔE 's are the electronic ligand field transitions. Using the observed $\langle g \rangle$ value and the assigned ΔE values, ξ was calculated to be 65 cm^{-1} while g_{\perp} and g_{\parallel} were calculated to be 1.990 and 1.978 respectively. The free ion spin-orbit coupling constant for Cr^{5+} (380 cm^{-1}) is drastically reduced for CrO^{3+} (65 cm^{-1}) and was accounted for by the very strong oxygen to metal bonding.

The magnetic susceptibility of $\text{Rb}_2\text{CrOCl}_5$ was measured over the temperature range of $77^\circ - 318^\circ\text{K}$. The theoretical expression for magnetic susceptibility given by Van Vleck²⁹ is $\chi = (C/T) + \chi_{\text{H.F.}}$ where C is the Curie constant and $\chi_{\text{H.F.}}$ is the temperature-independent contribution to the susceptibility. By using the experimentally determined g value and the ΔE 's from the spectral data for $\text{Rb}_2\text{CrOCl}_5$, C and $\chi_{\text{H.F.}}$ are calculated and give a χ value as indicated in equation 4. From the experimental plot of χ vs

$$\chi = 0.370/T + 55 \times 10^{-6} \quad \dots 4$$

($1/T$) for $\text{Rb}_2\text{CrOCl}_5$ one obtains $\chi = 0.536/T$ which is in very poor agreement with equation (4). This was attributed to the fact that $\text{Rb}_2\text{CrOCl}_5$ is unstable toward disproportionation to give Cr^{3+} and Cr^{6+} species.

Kon³⁰ postulated the existence of Cr^{5+} compounds in

²⁹Van Vleck, J.H., "Electric and Magnetic Susceptibilities", Oxford University Press, 1932.

³⁰Kon, H., Bull. Chem. Soc. Japan, 35, 2054 (1962).

CrO_3 - H_2SO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ - H_2SO_4 systems to explain the narrow ESR absorption lines he observed in these systems. The ESR spectra consisted of four narrow lines with uneven intensities with the line widths being 1 to 5 gauss. These same features were observed in the ESR spectra during the reduction of CrO_3 or $\text{K}_2\text{Cr}_2\text{O}_7$ with a variety of other acids such as trifluoroacetic, oxalic, lactic, or citric acid. However, attempts to isolate the paramagnetic species were unsuccessful.

In marked contrast to this, Carrington, et al.³¹ who were the first to observe the ESR spectrum of CrO_4^{3-} , reported the ESR signal to consist of a single line which could only be observed at $T = 20^\circ\text{K}$. The line width of the ESR signal is temperature dependent and increases rapidly as the temperature increases above 20°K . Swalen and Ibers²⁵ reported the ESR spectrum of peroxychromate ion, Cr(V)O_8^{3-} , and determined the line width by numerical analysis to be 23.5 gauss.

Striking differences in the temperature at which ESR starts to be observable was noted by van Reijen, et al.³² and this was thought to be connected with spin lattice relaxation. For Cr^{5+} in tetrahedral coordination, as in $\text{Ba}_3(\text{CrO}_4)_2$, they found that

³¹Carrington, A., Ingram, D.J.E., Schonland, D., and Symons, M.C.R., J. Chem. Soc., 4710 (1956).

³²van Reijen, L.L., Cassee, P., and van Haren, H.J., J. Chem. Phys., 38, 572 (1963).

resonance only occurs well below 80°K with a line width of approximately 50 gauss. For $(\text{NH}_4)_2\text{CrOCl}_5$ (octahedral) and K_3CrO_8 (dodecahedral) a line width of about 50 gauss was observed at room temperature.

Kon³³ presented detailed results of ESR, visible and infrared absorption measurements of complexes of the type RCrOCl_4 (R = pyridinium, quinolinium, or tetramethylammonium ion) and K_2CrOCl_5 in solution and in the solid state. In the infrared region he reported the strong band at 950 cm^{-1} in KBr pellet to be the Cr-O stretching vibration in all the complexes. The visible absorption spectra of the complexes were observed in nitrobenzene solution at room temperature and were reported to be almost identical, with absorption bands being observed at 18.00, 22.40(sh), and 23.50kK. The ESR spectra of these complexes in solution at room temperature and at 77°K were also virtually identical in their g values, line widths, and the average hyperfine splittings due to the ^{53}Cr isotope (natural abundance = 9.55%, with nuclear spin of $3/2$) as shown in Table II. Since all the complexes exhibit essentially the same ESR and visible absorption spectra, apparently the same paramagnetic species exist in solution. A reasonable structure of the common paramagnetic species was assumed

³³Kon, H., J. Inorg. Nucl. Chem., 25, 933 (1963).

TABLE II

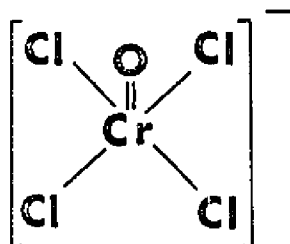
g-VALUES, LINE WIDTHS AND AVERAGE HYPERFINE SPLITTINGS
 OF RCrOCl_4 AND K_2CrOCl_5 IN SOLUTION AT ROOM
 TEMPERATURE ACCORDING TO KON³³

Sample	$\langle g \rangle$	Line Width (G)	Ave. hfs (G)
K_2CrOCl_5	1.9877	2.8*	19.7
RCrOCl_4			
R = pyridinium	1.9877	2.8* 2.1**	19.9
R = quinolinium	1.9880	2.6* 2.0**	19.9
R = $(\text{CH}_3)_4\text{N}^+$	1.9875	2.7* 1.9**	19.8

* In glacial acetic acid

** In nitrobenzene

to be a tetragonal pyramid:



The estimated values of $g_{||}$ and g_{\perp} were 2.008 and 1.974 from which a g average was calculated to be 1.985. This value is in approximate agreement with the observed values in solution. Kon explained the g values on the basis of molecular orbital theory assuming a considerable amount of covalency between the chromium and the chlorines.

In a later publication, Kon and Sharpless³⁴ recalculated g_{\perp} and $g_{||}$ by doing a line shape analysis to improve their accuracy. They carried out the calculation from the ESR of K_2CrOCl_5 enriched with ^{53}Cr (98%) in acetic acid at 77°K. The peaks due to Cr nuclear spin coupling were well separated from each other and $g_{||}$ and g_{\perp} were calculated to be 2.008₅ and 1.977₃, respectively. The same procedure was used for powdered $pyH(CrOCl_4)$ where $g_{||}$ and g_{\perp} were calculated to be 1.988₃ and 1.979₂. The agreement between the experimental and computed line shape for the powdered $pyH(CrOCl_4)$

³⁴Kon, H., and Sharpless, N.E., J. Chem. Phys., 42, 906 (1965).

was very good. Note that $g_{||}$ is greater than g_{\perp} in both cases with $g_{||}$ being greater than the free spin value (2.0023) in the case of the CrOCl_5^{2-} species.

A perturbation calculation carried through the second order using the Abragam-Pryce perturbation Hamiltonian was used to calculate the bonding parameters. In the second order, the electronic transition involving the transition of an electron in the filled b_1 bonding molecular orbital to the half-filled b_2^* orbital was taken into account. Kon and Sharpless assigned the electronic band observed at 18.30kK to the $b_1 \rightarrow b_2^*$ transition and showed by calculation that if the excited configuration, $b_1 \rightarrow b_2^*$, was neglected in equation 5 no physically acceptable solution for α (covalent bonding parameter) was possible regardless of the choice of the spin-orbit coupling parameter. The overall arrangement of the molecular orbital energy diagram was assumed to be the same as that given by Gray and Hare²⁷ except that the in-plane π bond involving $3d_{xy}$ is taken into account and the location of the bonding b_1 orbital may be much higher than in other isoelectronic complexes. From the values obtained for the calculated bonding parameters they concluded that a significant amount of π bonding between the chromium and oxygen is occurring and the in-plane π bond involving the $3d_{xy}$ metal orbital appears to be important in understanding the bond situation. The equations used to calculate the bonding parameters included the two indicated

below. Note that the shift of $g_{||}$ due to the $b_2^* \rightarrow b_1^*$ transition is

$$(g_{||}/2.0023) - 1 = -(1/E_{(b_2^*-b_1^*)})(2\alpha\beta_1\xi_m - \alpha'\beta_1'\xi_\ell) \pm (2\alpha\beta_1 - 2\alpha'\beta_1') \\ + (1/E_{(b_1-b_2^*)}) \pm (2\alpha'\beta_1\xi_m + \alpha\beta_1'\xi_\ell)(2\alpha'\beta_1 + \alpha\beta_1') \dots 5$$

$$(g_{\perp}/2.0023) - 1 = -\xi\beta_2^2/E_{(b_2^*-e^*)} \dots 6$$

positive in equation 5 but the $b_2^* \rightarrow b_1^*$ transition is not involved in equation 6. This, of course, would account for $g_{||}$ being greater than g_{\perp} in this case. This type of transition is usually ignored in metal complexes with less than five d electrons since the excitation energy from the bonding orbitals is usually too high to give a substantial contribution to the g factor.

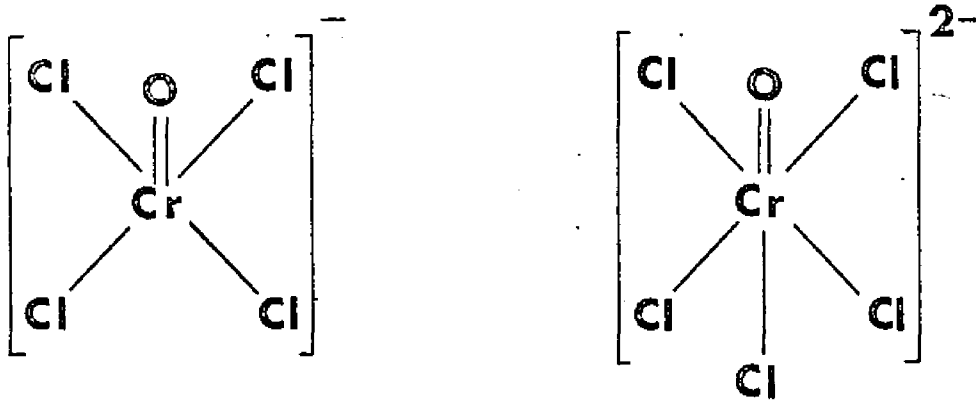
Kon and Sharpless³⁵ showed that the super hyperfine splitting in the ESR spectrum of CrOCl_5^{2-} solution at 77°K (in acetic acid saturated with HCl) was due to the ^{35}Cl and ^{37}Cl nuclei. The evidence given for this was obtained by studying the complex enriched (99.8%) with the even isotope, ^{52}Cr , in which the ESR spectrum showed a better resolved structure than with the non-enriched Cr complex.

Lipatova and Semenova³⁶ have studied the infrared spectra

³⁵Kon, H., and Sharpless, N.E., J. Chem. Phys., 43, 1081 (1965).

³⁶Lipatova, I.P., and Semenova, E.I., Teoreticheskaya Eksperimental'naya Khimiia, 2, 279 (1966).

of chromyl complexes of the type RCrOCl_4 ($\text{R} = \text{C}_5\text{H}_5\text{NH}^+$ or $\text{C}_9\text{H}_7\text{NH}^+$) and R_2CrOCl_5 ($\text{R} = \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+, \text{C}_9\text{H}_7\text{NH}^+$) in conjunction with the ESR spectra. In acetone and acetonitrile two narrow intense bands were observed at 1020 and 948 cm^{-1} for all complexes, with the 1020 cm^{-1} band as well as the ESR signal disappearing upon the addition of PbO_2 . They assumed partial oxidation takes place in solution and assigned the 1020 cm^{-1} band to the pentavalent chromium-oxygen stretching frequency and the band at 948 cm^{-1} to a chromium oxygen stretch due to sexivalent chromium. Since the 1020 cm^{-1} band was unchanged for all the complexes in either solvent, they postulated that the first coordination sphere of the chromyl chloride complexes in solution were all the same. In petroleum oil mull RCrOCl_4 had an intense band at 1015 cm^{-1} while R_2CrOCl_5 had a maximum in the $940 - 960\text{ cm}^{-1}$ region depending on the cation. This difference in the chromium-oxygen stretching frequency was explained by the effect of the chlorine attached trans to the chromyl oxygen assuming that the structures of the two species are



The ESR spectra of these complexes also differ in that the width of the paramagnetic absorption line for RCrOCl_4 is almost half that of R_2CrOCl_5 . In KBr pellet the RCrOCl_4 shows an intense band at 955 cm^{-1} but the ESR signal also disappeared. The apparent reason for this behavior was given as being due to the bromide entering the trans position to the chromyl oxygen, and the oxidation of Cr(V) to Cr(VI) during the grinding process in preparation of the pellet. Apparently, they assumed that air oxidation was occurring although this was not stated. The spectra of R_2CrOCl_5 in which there is no trans position available for occupancy by bromide are identical in petroleum oil mull and KBr pellet.

Brown³⁷ reported X-ray diffraction, magnetic susceptibility and infrared studies for cesium oxochloro complexes of the type, $\text{Cs}_2\text{M}^{(\text{V})}\text{OCl}_5$ ($\text{M}^{(\text{V})} = \text{Nb, Cr, Mo, or W}$). The structure of these compounds was reported to be the K_2PtCl_6 structure with the unit cell dimension of the chromium complex given as 10.24\AA . The magnetic susceptibility of $\text{Cs}_2\text{CrOCl}_5$ was determined in the temperature range from $89^\circ - 300^\circ\text{K}$ and the Curie-Weiss relation was obeyed for a small value of θ (Weiss constant). The magnetic susceptibility value was 1.80 B.M. which is very close to the spin-only value. In the infrared region the chromium-oxygen stretching vibration was reported at 925 cm^{-1} with the chromium-chlorine vibration occurring

³⁷Brown, D., J. Chem. Soc., 4944 (1964).

at 336 cm^{-1} for the chromium complex.

Mishra and Symons³⁸ presented evidence for a Cr(V) complex as a product of the reaction between 65% oleum and potassium chromate. The evidence consisted of the quantitative evolution of oxygen in accord with the reaction $-4\text{Cr}^{6+} \rightarrow 4\text{Cr}^{5+} + \text{O}_2$, ESR spectra, electronic spectra, and magnetic susceptibility measurements which were in accord with one unpaired electron. Electronic transitions were observed at 13.70kK ($\epsilon = 60$) and 18.10kK ($\epsilon = 40$). A possible formula for the Cr^{5+} complex was given as $\text{OCr}(\text{HS}_2\text{O}_7)_3$ but it was not isolated.

The Ballhausen-Gray molecular orbital scheme²⁶ was used by Mishra and Symons to assign the d-d electronic transitions that were observed. The band at 13.70kK was assigned as the $d_{xz}, d_{yz} \leftarrow d_{xy}$ and the second band at 18.10kK was assigned as the $d_{x^2-y^2} \leftarrow d_{xy}$ transition. They suggest that the hydrogen pyro-sulfate and possibly hydrogen sulfate are weakly bonded to transition metal ions both with respect to σ and π interactions compared to the pentachloro-derivative, CrOCl_5^{2-} , and, therefore, the first transition should be at slightly higher energies. The antibonding level involving the d_{xy} orbital will be raised in energy as a result of π -bonding with chloride while the d_{xz}, d_{yz} level which is already involved in π -bonding to oxygen will change very little in going from the

³⁸Mishra, H.C., and Symons, M.C.R., J. Chem. Soc., 4490 (1963).

chloro-complex to the oleum derivative since the $d_{x^2-y^2}$ orbital, which is an antibonding σ -orbital, would be expected to be raised in energy on going to the pentachloro-derivative. By use of the spectral data they calculated $g_{||}$ and g_{\perp} to be 1.93 and 1.98 respectively, while the observed values were 1.951 and 1.970 for the 65% oleum- $K_2Cr_2O_7$ solution.

The existence of $CrOF_5^{2-}$ in a 20% HF solution containing CrO_3 was reported by Garif'yanov³⁹. The ESR spectrum of this solution at 240°K was split into 5 components with a 6 gauss separation between each component. This splitting was interpreted as being derived from four equivalent ^{19}F nuclei and due to the interaction of the lone 3d electron with the strongly covalently bound ^{19}F nuclei. Observation of the ESR spectrum of this solution at 77°K showed a complex fluorine anisotropic super hyperfine structure. The ESR spectrum observed was similar to that of $MoOF_5^{2-}$ and hence the structure was thought to be the same in which the Cr^{5+} is located within an octahedron formed from five covalently bound atoms: 4 equivalent fluorine atoms and one oxygen atom, with the fifth fluorine in the trans position with respect to the oxygen having a weaker bond. The reported g value with respect to the central line was 1.960.

VanKemenade, Verbeek, and Cornaz⁴⁰ observed the ligand

³⁹Garif'yanov, N.S., Dokl. Akad. Nauk SSSR, 155, 385 (1964).

⁴⁰Van Kemenade, J.T.C., Verbeek, J.L., and Cornaz, P.F., Rec. Trav. Chim., 85, 629 (1966).

hyperfine structure in the ESR spectrum of CrOF_5^{2-} prepared in solution from $(\text{pyH})_2 \text{CrOCl}_5$ in 38% HF at 123°K . The optical spectrum of this solution in the region of $10,000\text{--}35,000 \text{ cm}^{-1}$ showed complete conversion to the fluoride compound had taken place. The color of the HF solution was pale yellow while the chloride complex was dark purple. The general shape of the spectrum was the same as that for $\text{MoO}(\text{OH})_3$ dissolved in 38% HF at 123°K .

Verbeek and Cornaz⁴¹ proposed a simple model for the observed ligand super hyperfine structure in complexes of the type MOX_5^{2-} where $\text{M} = \text{Cr}, \text{Mo}, \text{or W}$ and $\text{X} = \text{F}, \text{Br}$. They assumed that contact interaction and dipole-dipole interaction between the unpaired electron and the ligands are the origin of the ligand superhyperfine structure. It is shown that a remarkable resemblance exists between the spectrum based on these assumptions and the actual spectrum of a frozen solution of CrOF_5^{2-} in 38% HF.

Abdrakhmanov, Garif'yanov, and Semenova⁴² recently reinvestigated the ESR spectrum of CrO_3 in HF over the frequency range of 600-1200 Mcps. The ESR spectrum at 77°K consisted of seven partially resolved lines of superhyperfine structure from the four ^{19}F nuclei with $g_{\text{eff.}} = 1.96$ for the central line of the spectrum. Since one should only observe five lines from 4 equivalent

⁴¹Verbeek, J.L., and Cornaz, P.F., Rec. Trav. Chim., 86, 209 (1967).

⁴²Abdrakhmanov, R.S., Garif'yanov, N.S., and Semenova, E.I., Zhurnal Strukturnoi Khimii, 9, 530 (1968).

^{19}F nuclei they interpreted the seven lines observed as being due to the unpaired 3d electron of the central atom interacting with two magnetically non-equivalent pairs of ligand nuclei located in the equatorial plane of the complex. In the presence of covalent bonds of an unpaired electron with two non-equivalent pairs of ligand nuclei, nine superhyperfine structure lines should be observed, but they proposed that a partial superposition of the lines occurs reducing the number to seven and explaining the large width of the superhyperfine structure components. No additional hyperfine structure was observed in the frozen solution from the ^{19}F nuclei in the axial position which they explained was due to the magnitude of the hyperfine splitting lying within the limits of the line width of the individual superhyperfine structure from the fluorine atoms in the equatorial plane of the complex.

Manoharan and Rogers⁴³ also recently observed the superhyperfine interaction of ^{19}F in CrOF_5^{2-} . They prepared KCrOF_4 by the method of Clark and Sadana⁵, dissolved it in 48% HF and recorded the spectrum at 270°K and 77°K. The ESR at 270°K showed that the central line due to the unpaired electron was split into five equidistant lines with intensity ratios of 1:4:6:4:1 similar to that reported by Garif'yanov but more symmetric. As the concentration of KCrOF_4 was decreased by adding more HF the intensity ratios changed and each line was split into a doublet due to the interaction of the

⁴³Manoharan, P.T., and Rogers, M.T., J. Chem. Phys., 49, 5510 (1968).

unpaired electron with an axial fluorine. One of the components of each doublet appears more intense in the spectrum because the single line from the CrOF_4^- species, which shows no axial fluorine interaction, coincides with that component of the doublet due to the CrOF_5^{2-} species. However, they were not able to observe a spectrum of CrOF_5^{2-} alone on further dilution. Also, their efforts to obtain an ESR spectrum of a single crystal of $\text{K}_2\text{NbOF}_5 \cdot \text{KHF}_2$ containing K_2CrOF_5 were not successful. The frozen acid-glass spectrum that was observed for KCrOF_4 was similar to the one reported by Verbeek and Cornaz⁴¹ and by Garif'yanov³⁹. In Table III listed below the ESR data is recorded.

TABLE III

VALUES OF $g_{||}$, g_{\perp} AND $\langle g \rangle$ FOR CrOF_4^- AND CrOF_5^{2-} SPECIES
IN SOLUTION AND FROZEN GLASS

Parameter	CrOF_4^-	CrOF_5^{2-}	Reference
$g_{ }$	1.959	1.959	43
g_{\perp}	1.968	1.968	43
$\langle g \rangle$	1.964	1.963	43

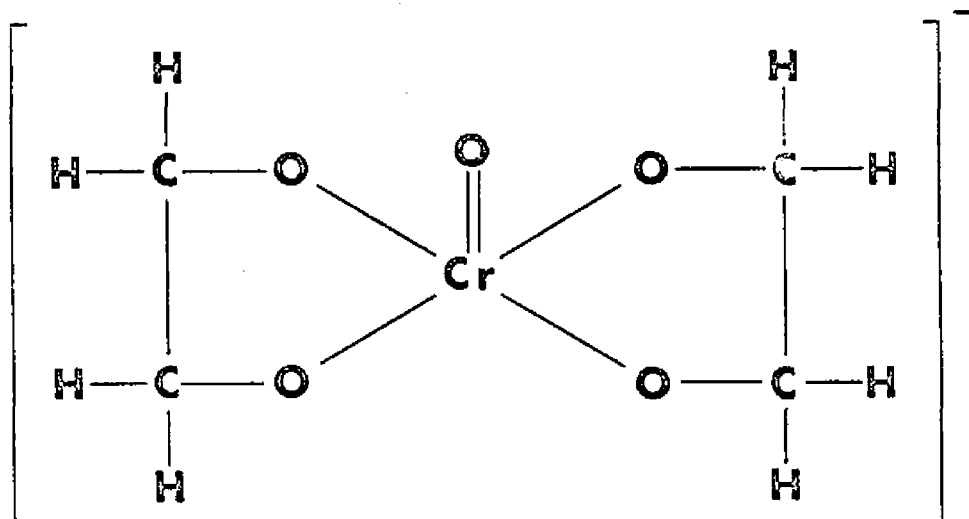
In most complexes containing MO^{n+} ($M = \text{V}, \text{Mo}, \text{or Cr}$) $g_{||} < g_{\perp}$. However, for CrOCl_5^{2-} and MoOCl_5^{2-} it was found that $g_{||} > g_{\perp}$ and this reversal must be reflected in their bonding.

Kon and Sharpless³⁴ explained this reversal by assuming a relatively low lying excited electronic configuration in which an electron in a filled b_1 orbital is excited to the half-filled b_2^* orbital. However, Manoharan and Rogers⁴³ proposed that it is the spin-orbit interaction of the ligand that is causing the reversal of the relative magnitudes of $g_{||}$ and g_{\perp} . By using the argument that λ_{Cl} is much higher than λ_F (λ = spin-orbit coupling constant) this would explain why $g_{||} < g_{\perp}$ in $MoOF_5^{2-}$ and $CrOF_5^{2-}$ but $g_{||} > g_{\perp}$ in $MoOCl_5^{2-}$ and $CrOCl_5^{2-}$.

Evidence for the existence of a Cr(V) complex with ethylene glycol was presented recently by Garif'yanov, Kozyrev, and Fedotov⁴⁴ from ESR data. The ethylene glycol complex of Cr(V) was obtained through warming of an ethylene glycol solution of either $(NH_4)_2CrO_4 - K_2CrO_4$ or $CrO_3 - K_2Cr_2O_7$ and its ESR spectrum determined in both liquid and solid solutions. The measurements were made through a temperature range of $320^\circ - 77^\circ K$ and in the liquid solution four lines were observed for the odd isotope and one for the even isotopes. Superimposed on this was a nine line spectrum with equal spacings of 0.64 gauss which was attributed to the protons of the complex. Spectra of the solid solutions at $218^\circ K$ showed the even isotopes to produce a single line with $g = 1.981$ and a line width of 7.8 gauss. The ^{53}Cr isotope had an anisotropic hyperfine behavior and $A_{||}$ was 35 gauss while A_{\perp} was calculated to be 8.9 gauss. From

⁴⁴Garif'yanov, N.S., Kozyrev, B.M., and Fedotov, V.N., Dokl. Akad. Nauk SSSR, 178(4), 808 (1968).

the data obtained they proposed the structure given below.



From the foregoing (exhaustive) discussion it would appear that the preparative and other studies recorded in the literature of Cr(V) complexes are generally quite incomplete. For example the few spectral studies of the existing chloro derivatives of Cr(V), namely RCrOCl_4 and R_2CrOCl_5 , are incomplete and even contradictory. Therefore, it seemed that a reinvestigation of the existing species as well as preparative and physical-chemical studies of new species would be beneficial. Such a study would allow one to make a more complete assignment of the electronic spectral data, and then interesting and revealing comparisons could be made with $\text{VO}^{2+}(\text{d}^1)$ and $\text{MoO}^{3+}(\text{d}^1)$, both of which exhibit many and a variety of complexes.

EXPERIMENTAL DETAILS AND RESULTS

(A) Apparatus and Procedures

1. Elemental Analyses

Carbon and hydrogen analyses were performed by Mr. R.L. Seab of this department using a carbon-hydrogen analyzer manufactured by Coleman Instruments Corp., Maywood, Illinois. Chloride analyses were done either by the author or by Galbraith Laboratories at Knoxville, Tennessee. All other elemental analyses were done by Galbraith Laboratories.

Chloride analyses performed in this laboratory were done by the Volhard method. In order to observe the endpoint in the Volhard titration the chromium was removed prior to the titration by precipitating it as PbCrO_4 and filtering the precipitate from a hot solution. The standardized silver nitrate was also added to the sample when it was hot to prevent the co-precipitation of PbCl_2 .

2. Infrared Spectra

Infrared spectra ($4000 - 300 \text{ cm}^{-1}$) were recorded using a Beckman model IR-10-spectrophotometer. A scan of polystyrene film was employed for calibration and the wavenumber accuracy is specified to be $\pm 4 \text{ cm}^{-1}$. The spectra were run as Nujol mulls pressed between cesium iodide plates and in some cases as KBr or KCl pellets.

3. Equivalent Conductances

The resistance of solutions having a concentration range of $10^{-3} - 10^{-4} \text{ M}$ were measured in a conductivity cell by means of a

model RC 16 conductivity bridge manufactured by Industrial Instruments. The solvent used was acetonitrile and measurements were made at room temperature.

4. Magnetic Susceptibilities

a. Gouy Method: The sample was packed into a glass tube which was about 18 cm long and had an outside diameter of 5 mm by tapping the end of the tube lightly on the bench. The two ends of the glass tube were separated by a glass partition in the middle of the tube and the lower end was sealed. The sample tube was suspended such that one half of the tube hung below the center of the magnet and one half above so as to partially eliminate any correction due to the tube itself. A draft tube was used around the sample tube to eliminate any disturbance due to air currents. A thermometer in the balance case allowed for the determination of temperature.

The balance used was an Ainsworth type BCT with magnetic damping. A model AL7500 electromagnet produced by Alpha Scientific Laboratories, Inc., Berkeley, California, provided the magnetic field for the samples. The magnet contained 4 inch pole caps with an air gap of approximately $1\frac{1}{2}$ inches. The magnetic field was controlled by a variable output power supply which was adjusted to a current of 8 amps; and it provided a magnetic field of approximately 6000 gauss. The magnet was air cooled and hence the current was applied intermittantly to prevent overheating and change in field strength.

b. NMR Method: The NMR spectra were recorded on a Varian A60-A NMR Spectrometer. A special coaxial tube, which was composed of a small tube centered inside a larger tube, was purchased from Wilmad Glass Company, Buena, New Jersey. Both the inner and outer tubes are closed at one end and the inner tube is centrally held by a movable glass spacer. The pure solvent which was either acetonitrile or methylene chloride was placed in the inner tube and the solution composed of the solvent and the paramagnetic species was placed in the annulus formed by the small and larger tubes. The solvent for the inner tube and the outer tube were identical except for the paramagnetic species. The spectra were recorded at a sweep of 50 cps in order to sufficiently spread out the solvent peak in the diamagnetic solvent from the solvent peak in the paramagnetic solution. The concentration of the paramagnetic solution was ordinarily about 20 mgs. of solute in 5 ml. of solution.

5. Optical Spectra

The optical spectra were recorded by means of a Cary 14 Spectrophotometer. Solution spectra were recorded by use of a set of one cm matched quartz cells. Five cm matched quartz cells were used when the solubility was very low. A base line of solvent vs solvent was run in all cases in order to eliminate any spurious bands due to the solvent. Reagent grade solvents were used without any further purification.

Solid state spectra were run in KBr pellet, KCl pellet, and in Nujol mulls. Pellets were prepared in a dry bag under an argon

atmosphere by means of a Mini-Press purchased from Wilks Scientific Corporation. The pellet was then placed into the cell compartment of the Cary 14 Spectrophotometer which was flushed with dry nitrogen before and during the run. Pellets were also prepared in the conventional manner with a hydraulic press.

Nujol mulls were prepared in a dry bag when necessary with the sample being smeared on filter paper which in turn was taped to a holder. The spectra were recorded while the sample was under a dry nitrogen atmosphere.

Low temperature spectra were recorded of Nujol mulls smeared on filter paper. The sample was taped onto a brass holder which fit into an optical dewar flask with walls of quartz. The samples were originally placed beneath the surface of the liquid nitrogen. After sufficient time had elapsed for temperature equilibrium to occur the liquid nitrogen was poured off so that the level was just below the light path. In this manner interference was prevented from the bubbling of the liquid nitrogen and better resolution was obtained. A baseline of Nujol vs Nujol on filter paper was also run to eliminate any bands due to the Nujol or to impurities present in Nujol.

A diffuse reflectance spectrum was observed for one compound by means of a point by point plot of the optical density which was recorded on a Beckman DU single beam spectrophotometer. Magnesium carbonate was used as a reference.

6. Electron Paramagnetic Resonance Spectra

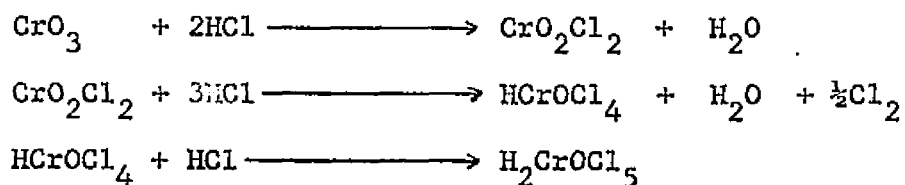
The ESR spectra of all the samples were recorded using a model JES-3BX, X band spectrometer produced by the Japan Electron Optics Laboratory Co., Ltd., Tokyo, Japan. All spectra were recorded at ambient temperature as the first derivative on an xy recorder manufactured by the Riken Denshi Co., Ltd., Tokyo, Japan, model XY-D5N. The magnetic field applied to the sample was measured by means of a gaussmeter.

(B) Preparation of Compounds

The reagents used in the preparation of these compounds were of reagent grade and were purchased from available commercial sources. These reagents were used without further purification.

1. Chloro-Complexes

The chloro-complexes were prepared by the method of Weinland and Fiederer¹. In this procedure CrO_3 was dissolved in a solution of glacial acetic acid that was saturated with hydrogen chloride to reduce Cr(VI) to Cr(V). According to the spectrophotometric studies of Krauss and Muenster⁹ the reduction may take place by the following steps:



In a second solution of glacial acetic acid saturated with hydrogen chloride, the chloride salt of the appropriate cation was dissolved. These two solutions were poured together and precipitation of the chloro-complex of the oxochromium(V) species occurred. Some of the precipitates formed immediately while others formed slowly. However, complete precipitation seemed to occur in at least one hour. The precipitate was then vacuum filtered, washed with glacial acetic acid under an inert atmosphere (nitrogen or argon), and dried under vacuum for approximately 48 hours. Some of the prepared complexes were then recrystallized from appropriate solvents to effect further purification. The $\text{Rb}_2\text{CrOCl}_5$ and $\text{Cs}_2\text{CrOCl}_5$ were prepared previously by Weinland and Fiederer²; $\text{Me}_4\text{NCrOCl}_4$ was previously reported by Kon³³ but the remaining complexes had not been prepared prior to this work.

a. $\text{Rb}_2\text{CrOCl}_5$, Rubidium oxopentachlorochromate(V): Since RbCl is not very soluble in acetic acid this compound cannot be prepared conveniently in a very large yield. It is not soluble in any of the common organic solvents and decomposition appears to occur in such solvents as dimethylsulfoxide and dimethylformamide. Upon heating, this complex changes from a deep red to a lighter red color at approximately 200°C but no further changes take place below 260°C . Decomposition takes place very slowly at room temperature, even while storing under argon. No change in color was observed during this period of time. The decomposition could result from disproportionation

of the Cr(V) to Cr(VI) and Cr(III) or possibly by an oxidation-reduction reaction occurring between the Cr(V) and the chloride coordinated to the chromium, resulting in the formation of a Cr(III) species and elemental chlorine although no chlorine odor could be detected. The magnetic susceptibility increased from 1.92 to 2.74 B.M. over a period of approximately four months.

Calculated for $\text{Rb}_2\text{CrOCl}_5$: %Cl 42.60; Found: %Cl 42.82

b. $\text{Cs}_2\text{CrOCl}_5$, Cesium Oxopentachlorochromate(V): The stability of this complex appears to be greater than that for the corresponding rubidium complex. However, precautions need to be taken to avoid the presence of moisture and oxygen for extended periods of time. The cesium complex is insoluble in all common non-polar solvents, only slightly soluble in solvents such as acetonitrile, nitromethane, and quite soluble in dimethylformamide and dimethylsulfoxide with decomposition taking place in a short time as the color changes from yellow-red to green. Upon heating it appears to change from a wine red to a lighter red at approximately 190°C and no further changes occur up to 260°C .

Calculated for $\text{Cs}_2\text{CrOCl}_5$: %Cl 34.70; Found: %Cl 33.36.

c. $\text{Me}_4\text{NCrOCl}_4$, Tetramethylammonium Oxotetrachlorochromate(V): When exposed to the atmosphere this compound rapidly changed from a dark red to an orange yellow with hydrolysis apparently taking place. Attempts to purify the product in the original preparation by

recrystallization from acetonitrile resulted in the formation of a violet precipitate. The compound which resulted was a Cr(III) species with a probable formula of $(\text{Me}_4\text{N})_2\text{Cr}(\text{H}_2\text{O})\text{Cl}_5$. Recrystallization from methylene chloride did not result in the formation of a Cr(III) complex and a slight improvement was effected in the elemental analysis, but the chloride analysis was still not at an acceptable value, as indicated below. Possibly another recrystallization would have improved the chloride analysis to an acceptable level.

Solutions of CrO_3 in 6M HCl readily form precipitates⁴⁵ with large alkylammonium ions, indicating CrO_3Cl^- salts may generally be prepared by this simple precipitation technique. The infrared spectrum shows a band at 910 cm^{-1} (medium) which was assigned as the Cr-O symmetric stretch by Tuck and Faithful⁴⁶. The infrared spectrum of the precipitate obtained in the preparation of $\text{Me}_4\text{NCrOCl}_4$ showed a weak band at 910 cm^{-1} possibly indicating that some of precipitate may have been $\text{Me}_4\text{NCrO}_3\text{Cl}$ which could account for the slightly high carbon-hydrogen analysis and also the low chloride analysis. No change appears to take place in this compound upon heating to 260°C .

Calculated for $\text{Me}_4\text{NCrOCl}_4$: %C 16.92; %H 4.26; %N 4.93; %Cl 49.93; Found %C 17.57; %H 5.24; %N 4.09; %Cl 44.42.

⁴⁵Haight, G.P., Richardson, D.C., and Coburn, N.H., Inorg. Chem., 3, 1777 (1964).

⁴⁶Tuck, D.G., and Faithful, B.D., J. Chem. Soc., 5753 (1965).

d. Et₄NCrOCl₄, Tetraethylammonium Oxotetrachlorochromate(V): A crystalline red precipitate of this compound was obtained in rather pure form. Recrystallization of this compound from acetonitrile did not result in the formation of a Cr(III) species, contrary to the result with Me₄NCrOCl₄. It appears much more stable to atmospheric conditions than the tetramethylammonium complex. It also changes color but over a much longer period of time. It is quite soluble in most polar solvents such as acetonitrile, nitromethane, etc., slightly soluble in CH₂Cl₂ but insoluble in non-polar solvents. Decomposition of this complex takes place at 150°C.

Calculated for Et₄NCrOCl₄: %C 28.23; %H 5.93; %N 4.13; %Cl 41.69; Found: %C 28.78; %H 6.30; %N 4.01; %Cl 40.09.

e. Pr₄NCrOCl₄, Tetrapropylammonium Oxotetrachlorochromate(V): The preparation of this compound results in the immediate formation of a yellow-gold precipitate. This compound is light sensitive which causes it to slowly turn from the yellow-gold to a light green. This type of decomposition does not take place when the compound is stored in a dark place, but it does slowly hydrolyze in the atmosphere turning to a bright yellow color. It is quite soluble in nitromethane and acetone, slightly soluble in acetonitrile, tetrahydrofuran, and methylene chloride, but insoluble in non-polar solvents. Decomposition of this compound takes place at 158°C.

Calculated for Pr₄NCrOCl₄: %C 36.39; %H 7.12; %N 3.54; %Cl 35.79; Found: %C 36.17; %H 7.30; %N 3.76; %Cl 34.30.

f. $(C_6H_5)_4AsCrOCl_4$, Tetraphenylarsonium Oxotetrachlorochromate(V):

This compound precipitated very slowly from the acetic acid solution in a brown-red crystalline form. To improve the purity of the compound it was necessary to recrystallize the product from methylene chloride. It is highly soluble in most polar solvents and insoluble in such non-polar solvents as benzene, carbon tetrachloride, etc. Compared to the other chromium(V) chloro complexes the rate of decomposition in the atmosphere appears to be the slowest. After sitting in the atmosphere for approximately 18 hours there was little change in color but the infrared data indicated that some decomposition had taken place. The compound decomposes when heated to approximately $190^{\circ}C$.

Calculated for $(C_6H_5)_4AsCrOCl_4$: %C 48.60; %H 3.40;
 %As 12.63; %Cl 23.91; Found: %C 48.36; %H 3.44; %As 13.34;
 %Cl 23.87.

g. $Bu_4PCrOCl_4$, Tetrabutylphosphonium Oxotetrachlorochromate(V):

A red crystalline precipitate formed in the preparation of this compound very similar in appearance to $Et_4NCrOCl_4$. No recrystallization was necessary since the elemental analysis of the original precipitate was very good. This compound decomposes in the atmosphere changing from a red to yellow color after sitting for approximately four hours. Decomposition does not appear to take place while the sample is stored in a dessicator. This particular species dissolves quite readily in polar solvents including chloroform and methylene

chloride and is also slightly soluble in benzene. This compound decomposes at approximately 110°C .

Calculated for $\text{Bu}_4\text{PCrOCl}_4$: %C 40.96; %H 7.74; %P 6.82; %Cl 30.22; Found: %C 40.61; %H 7.96; %P 6.79; %Cl 30.97.

h. $(\text{C}_6\text{H}_5\text{CH}_2)(\text{C}_6\text{H}_5)_3\text{PCrOCl}_4$. Benzyltriphenylphosphonium Oxotetra-chlorochromate(V): Precipitation of this product did not occur immediately, but after the reaction solution sat for a short time a brown precipitate began to form. Attempts to purify the product by recrystallization from methylene chloride were not successful. The analysis from the product obtained from recrystallization was in poorer agreement with the calculated values than was the original product. The high carbon-hydrogen analysis and low chloride analysis is indicative of the presence of a small amount of $(\text{C}_6\text{H}_5\text{CH}_2)(\text{C}_6\text{H}_5)_3\text{PCrO}_3\text{Cl}$. Decomposition of the compound takes place after it is exposed to the atmosphere for about four hours. It is soluble in most polar solvents including chloroform and methylene chloride, and is slightly soluble in benzene. This compound is the only one of the chloro complexes that melts before it decomposes. Its melting point occurs at $128 - 130^{\circ}\text{C}$ and it appears to decompose at approximately 135°C .

Calculated for $(\text{C}_6\text{H}_5\text{CH}_2)(\text{C}_6\text{H}_5)_3\text{PCrOCl}_4$: %C 53.30; %H 3.91; %P 5.68; %Cl 25.16; Found: %C 54.33; %H 4.20; %P 5.79; %Cl 23.05.

Attempts were made to reduce the CrO_3 to Cr(V) by adding a minimum amount of HCl (just enough to reduce the CrO_3) to a solution containing CrO_3 , 48% HF, and HOAc with the thought that if there was

not such a high concentration of chloride ion available the fluoride ion would have a better chance of coordinating to the Cr. This, however, was not successful due to the fact that it takes a fairly high concentration of HCl for the reduction of CrO_3 to take place.

Sulfur dioxide was tried as a reducing agent for CrO_3 but the CrO_3 was reduced all the way down to Cr(III) as was indicated by the change in color of the CrO_3 - HOAc solution from red to green as SO_2 was slowly bubbled into the solution.

Table IV lists the color and decomposition temperature of the oxochlorochromium(V) compounds prepared in this work.

2. Preparation of a Fluoro Complex

Other than by the direct fluorination of potassium dichromate with a halogen fluoride no fluoro complexes have been previously isolated, although numerous ESR spectral measurements have been reported of what were assumed to be fluoro oxochromium(V) species in solution.

Numerous attempts were made during the course of this study to prepare a fluoro complex. A similar procedure to that used for the chloro complex was tried with the modification of adding 48% HF to the acetic acid solution and using the fluoride salt of the desired cation rather than the chloride salt. However, with the acetic acid solution saturated with HCl this always resulted in the formation of a chloro complex. Without using HCl in the acetic acid solution the chromium was not reduced to Cr(V) and the product

TABLE IV

COLOR AND DECOMPOSITION TEMPERATURES OF OXOCHROMIUM(V) COMPLEXES

Compound	Color	Decomposition Temp.
$\text{Rb}_2\text{CrOCl}_5$	dark red	$>260^\circ\text{C}$
$\text{Cs}_2\text{CrOCl}_5$	dark red	$>260^\circ\text{C}$
$\text{Me}_4\text{NCrOCl}_4$	red	$>260^\circ\text{C}$
$\text{Et}_4\text{NCrOCl}_4$	red	150°C
$(\text{Pr})_4\text{NCrOCl}_4$	gold	158°C
$\text{Bu}_4\text{PCrOCl}_4$	red	110°C
$(\text{C}_6\text{H}_5)_4\text{AsCrOCl}_4$	red	190°C
$(\text{C}_6\text{H}_5\text{CH}_2)(\text{C}_6\text{H}_5)_3\text{PCrOCl}_4$	dark brown	$128-130^\circ\text{C}^{(a)}$

^aMelting point (it decomposes at 135°C).

formed was CrO_3F^- which precipitated with a large cation.

A method that was used with some success for the preparation of the fluoro complex was as follows. Approximately 0.3 grams of $\text{Et}_4\text{NCrOCl}_4$ was dissolved in about 15 ml. of methylene chloride under an argon atmosphere. To this solution an HF solution containing silver fluoride was added. A red precipitate formed and after stirring for 2 to 3 minutes the red methylene chloride solution turned yellow. The yellow solution was decanted off into a clean flask under argon and the solvent was evaporated off. As the evaporating process took place a small amount of green solid material formed on the side of the flask and again the solution was poured off into a clean container under an argon atmosphere. After complete evaporation a yellow precipitate was left which was very moisture sensitive. The HF solution of AgF was prepared by dissolving the Ag_2CO_3 obtained from 5 grams of AgNO_3 and excess Na_2CO_3 in 48% HF. The HF solution was evaporated down in a water bath until the AgF began precipitating. At this point it was added to the methylene chloride solution containing the $\text{Et}_4\text{NCrOCl}_4$.

Attempts to obtain a reproducible fluorine analysis on this compound were unsuccessful. Three different samples were submitted to a commercial laboratory for a fluorine analysis and the three values reported were 14.64%, 28.71% and 38.75%. The calculated value is 22.40%. On the three samples submitted for analysis the carbon, hydrogen and nitrogen analysis were very similar.

Calculated for $(\text{Et}_4\text{N})_2\text{CrOF}_5$: %C 45.40; %H 9.52; %N 6.60;
 Found: %C 46.37; %H 10.84; %N 6.15.

3. Preparation of $\text{Et}_4\text{NMoOCl}_4$, Tetraethylammonium Oxotetrachloro-
molybdate(V)

Two types of oxochloromolybdates(V), RMoOCl_4 and R_2MoOCl_5 , have been reported in the literature. Piovesana and Furlani⁴⁷ recently reported that the particular species one gets is dependent on the size of the cation. Since the tetraethylammonium salt of the chloro oxomolybdenum(V) species was prepared and used as a starting material by Pence⁴⁸ in preparing β -diketone derivatives of oxomolybdenum(V) complexes it seemed desirable to determine whether this starting material was $(\text{Et}_4\text{N})_2\text{MoOCl}_5$ as reported or $\text{Et}_4\text{NMoOCl}_4$ analogous to $\text{Et}_4\text{NCrOCl}_4$.

$\text{MoO}(\text{OH})_3$ was used as a source of Mo(V). This was prepared by the method of Bishop⁴⁹. The procedure mentioned by Palmer⁵⁰ for the synthesis of $(\text{NH}_4)_2\text{MoOCl}_5$ was adopted for the preparation of the oxochloromolybdenum(V) species by substituting the appropriate number of moles of tetramethylammonium chloride in place of $(\text{NH}_4)_2\text{CO}_3$. A green crystalline material which precipitated was washed and dried

⁴⁷Piovesana, O., and Furlani, C., Inorg. Nucl. Chem. Let., 3, 535 (1967).

⁴⁸Pence, H.E., Ph.D. Dissertation, Louisiana State University, Baton Rouge, Louisiana, 1968.

⁴⁹Bishop, A.D., M.S. Thesis, Louisiana State University, Baton Rouge, Louisiana, 1962.

⁵⁰Palmer, W.G., "Experimental Inorganic Chemistry", Cambridge University Press, Cambridge, England, 1954.

under vacuum. The elemental analysis indicated the compound was $\text{Et}_4\text{NMoOCl}_4$.

Calculated for $\text{Et}_4\text{NMoOCl}_4$: %C 25.02; %H 5.26; %N 3.65; %Cl 36.92; Found: %C 24.88; %H 5.22; %N 3.43; %Cl 34.62.

4. Attempts to Prepare a Bromo Complex

In an attempt to prepare a species containing a CrOBr_4^- or CrOBr_5^{2-} anion, a method similar to that used for the chloro complexes was tried. Forty milliliters of acetic acid was saturated with HBr and one gram of CrO_3 (0.01 moles) was dissolved in this solution. To another solution of acetic acid saturated with HBr 2.5 grams (0.012 moles) of Et_4NBr was added. When the two solutions were poured together a dark green solution resulted. When this solution was cooled in an ice bath orange crystals formed. Elemental analysis of this precipitate indicated that the product was a tribromide of the formula, Et_4NBr_3 . Care must be taken when HBr is bubbled into the acetic acid that an excess of moisture does not condense into the solution. This appears to prevent the orange crystalline product from precipitating.. The presence of water in a solution containing a tribromide leads to the equilibrium reaction, $\text{Br}_2 + \text{Br}^- \rightleftharpoons \text{Br}_3^-$, with the equilibrium constant being 17.4.⁵¹ The stability of a tribromide salt increases with increasing cationic size. In this preparation the tribromide precipitated

⁵¹Dubois, J., and Herzog, H., Bull. Soc. chim., 57 (1963).

immediately when $C_{16}H_{33}Me_3NBr$ was used but some difficulty was experienced when Et_4NBr was used. Presumably the difference, in part, was due to the size of the cation used.

Apparently, from the results obtained, HF is not a strong enough reducing agent while HBr is too strong of a reducing agent and reduces the chromium to a positive three state while being oxidized itself to a tribromide. Tribromides have been prepared before but this must be unique with regard to the method used.

The reflectance spectrum of Et_4NBr_3 was run using $MgCO_3$ as a reference. One maximum was observed at $440m\mu$. The visible-uv spectrum of this compound in acetonitrile showed one maximum at $268m\mu$ while $C_{16}H_{33}Me_3NBr_3$ exhibited a maximum at $275m\mu$ in acetonitrile.

Calculated for Et_4NBr_3 : %C 25.96; %H 6.86; %N 3.79; %Br 64.79; Found: %C 25.97; %H 7.13; %N 3.80; %Br 63.81.

Calculated for $C_{16}H_{33}Me_3NBr_3$: %C 43.51; %H 8.08; Found: %C 43.49; %H 8.41.

5. Attempted Preparation of Other Cr(V) Complexes

Compounds of the type $Et_4N[MoOCl_3(AA)]$, where AA represents a β -diketone such as dibenzoylmethane, benzoyltrifluoroacetone, etc., had been prepared by Pence⁴⁸ using $Et_4NMoOCl_4$ as a starting material. Hence, it seemed logical to try to prepare analogous compounds of chromium(V) using the β -diketone as chelating agents. However, the results obtained in these attempted preparations were far from

gratifying. $\text{Me}_4\text{NCrOCl}_4$, $\text{Et}_4\text{NCrOCl}_4$, and $\text{Cs}_2\text{CrOCl}_5$ were tried as starting materials. Numerous problems were encountered in selecting an appropriate solvent. Many solvents that were tried for $\text{Me}_4\text{NCrOCl}_4$ and $\text{Et}_4\text{NCrOCl}_4$ apparently caused decomposition (or disproportionation) of the complex as was evident from the solvent changing color from a dark red to a green. $\text{Et}_4\text{NCrOCl}_4$ did not appear to decompose in acetonitrile, tetrahydrofuran, or methylene chloride but upon addition of a chelating agent such as dibenzoylmethane the solution slowly turned green. $\text{Cs}_2\text{CrOCl}_5$ was slightly soluble in acetonitrile but this complex did not react with any of the β -diketones tried. Attempts to improve the situation by carefully drying the solvents, using the sodium salt of the β -diketones, and performing the reaction under an inert atmosphere were not fruitful.

Numerous other chelating agents were tried such as dipyridyl, o-phenanthroline, 8-hydroxyquinoline, tartaric acid and kojic acid, just to mention a few. In almost all cases there was either no reaction or a precipitate was isolated whose elemental analysis did not fit any reasonable molecular formula. If the analysis did fit some formula, the infrared data and magnetic susceptibility indicated that the product was a Cr(III) complex. Kojic acid appeared to react with $\text{Cs}_2\text{CrOCl}_5$ in a hot acetonitrile solution. The infrared data indicated that the kojic acid had complexed the chromium. Infrared band assignments of the kojic acid complexes of

Cu^{2+} , Zn^{2+} , Ni^{2+} , and Co^{2+} have recently been made by Murakami and Mera⁵². The C=O stretching frequency in kojic acid occurs at 1668 cm^{-1} and shifts to 1634 cm^{-1} in all of the four divalent ion complexes. The C=C stretching frequency in kojic acid gives rise to bands at 1636 , 1620 and 1589 cm^{-1} and these shift to 1575 and 1540 cm^{-1} in the divalent metal kojates. Ortego⁵³ reported the C=O stretching frequency at 1617 cm^{-1} in a U(IV) kojate complex and the C=C stretching frequencies at 1568 , 1515 and 1510 cm^{-1} . In the chromium complex a band at 1622 cm^{-1} was observed in the carbonyl region and bands observed at 1575 and 1520 cm^{-1} could certainly correspond to the C=C stretching frequencies. The magnetic susceptibility of the chromium complex was 1.78 B.M.; but the carbon-hydrogen analysis was much too low which probably indicates the reaction had not gone to completion even after proceeding for one week.

The reactions between $\text{Cs}_2\text{CrOCl}_5$ and hydroxy acids such as tartaric acid, hydroxy malonic acid, and malic acid was significant in that something other than a Cr(III) was obtained. These compounds were all prepared in a similar manner. Approximately a 10/1 mole ratio of hydroxyl acid/ $\text{Cs}_2\text{CrOCl}_5$ was necessary in order for the reaction to go to completion. The reaction was carried out in hot acetonitrile and enough solvent was used to completely dissolve the

⁵²Murakami, Y., and Mera, K., Bull. Chem. Soc. Japan, 39, 396 (1966).

⁵³Ortego, J., Ph.D. Dissertation, Louisiana State University, Baton Rouge, Louisiana, 1968.

hydroxy acid. The tartaric acid and hydroxy malonic acid complexes formed in about twenty-four hours whereas the malic acid complex appeared to take about 3 days. The precipitates that were obtained were filtered, washed several times with hot tetrahydrofuran and dried under vacuum. The data obtained from physical-chemical studies of these complexes will be discussed in a later section.

Calculated for $\text{Cs}_2\text{CrO}(\text{tart})\text{Cl}_3$: %C 8.15; %H 0.86; %Cr 8.82; %Cl 18.05; Found: %C 7.04; %H 1.23; %Cr 9.54; %Cl 18.33.

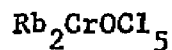
Calculated for $\text{Cs}_2\text{CrO}(\text{C}_3\text{H}_2\text{O}_5)\text{Cl}_3$: %C 6.43; %H 0.34; %Cl 19.09; Found: %C 7.74; %H 1.29; %Cl 21.20.

Calculated for $\text{Cs}_2\text{CrO}(\text{C}_4\text{H}_4\text{O}_5)\text{Cl}_3$: %C 8.46; %H 0.70; %Cl 18.60; Found: %C 9.46; %H 1.57; %Cl 19.51.

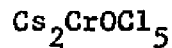
(C) Physical Chemical Data

1. Infrared Spectra

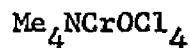
The recorded spectra are listed for each of the compounds in the region of $2000 - 300 \text{ cm}^{-1}$. The spectra were recorded with cesium iodide plates using Nujol mulls. Intensities are indicated by the abbreviations s-strong, m-medium, w-weak, sh-shoulder and v-very.



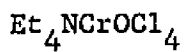
945(s), 360(sh), 340(sh), 320(vs)



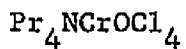
940(s), 340(vs), 320(sh)



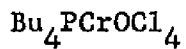
1420(m), 1285(w), 1022(sh), 945(s), 910(m), 425(sh), 400(vs), 350(sh)



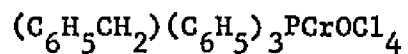
1420(w), 1200(w), 1185(s), 1105(w), 1080(w), 1070(m),
1040(s), 960(m), 910(w), 795(s), 750(sh), 410(sh), 395(vs), 360(sh).



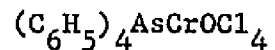
1345(m), 1290(w), 1190(m), 1055(m), 1040(s), 1005(s),
985(m), 965(m), 880(w), 770(s), 520(w), 410(sh), 400(vs), 350(w).



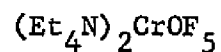
1230(s), 1190(w), 1100(s), 1085(sh), 1050(w), 1023(s),
1010(w), 970(m), 948(w), 905(s), 820(s), 695(w), 385(vs), 350(sh).



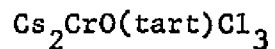
1490(sh), 1440(s), 1410(w), 1340(w), 1320(w), 1240(w),
1190(w), 1160(w), 1140(w), 1110(s), 1070(w), 1030(w), 1020(m),
1000(m), 940(s), 830(m), 785(s), 745(s), 720(s), 700(sh), 685(s),
575(m), 505(s), 490(s), 415(m), 370(m), 330(m), 300(w).



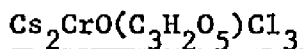
1460(s), 1360(m), 1200(m), 1180(m), 1105(s), 1085(sh),
1040(s), 1020(s), 970(w), 940(m), 765(s), 710(s), 485(sh), 475(s),
405(s), 375(sh), 360(s).



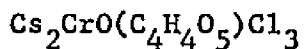
1380(w), 1200(sh), 1185(m), 1110(sh), 1070(s), 1050(sh),
1010(m), 960(s), 915(sh), 890(s), 800(s), 480(m), 450(m).



1750(s), 1635(m), 1425(w), 1320(w), 1240(m), 1200(m),
1140(m), 1110(m), 960(sh), 945(s), 830(m), 780(m), 740(m), 595(w),
540(w), 520(w), 470(w), 345(s), 320(sh).



1735(s), 1600(s), 1120(s), 950(sh), 930(s), 810(m), 770(m),
720(w), 550(w), 430(w), 330(s).



1735(s), 1590(s), 1270(w), 1190(m), 1105(m), 1080(m),
1040(w), 935(m), 630(w), 580(m), 430(w), 335(s), 305(sh).

A complete assignment of all bands recorded above would require extensive calculations (or a lot of guessing) and contribute very little to this work. However, it is of extreme interest for this research problem to assign the stretching frequencies of the Cr-O multiple bond and also the stretching frequencies of the Cr-Cl bond. Barraclough, Lewis and Nyholm⁵⁴ pointed out that the metal multiply bonded oxygen stretching frequency ordinarily lies in the region of 900 - 1100 cm^{-1} and that the intensity is usually greater than that of the bands due to any of the surrounding bands. Likewise it is possible from its high intensity to pick out the chromium-chlorine stretching frequencies. Nakamoto and Behnke⁵⁵ have used a normal coordinate analysis as a basis for assignments of bands in the compound, $\text{K}[\text{Pt}(\text{AA})\text{Cl}_2]$, and report two strong absorption bands at 339 and 327 cm^{-1} which correspond to the platinum-chlorine stretching frequencies.

⁵⁴Barraclough, C.G., Lewis, J., and Nyholm, R.S., J. Chem. Soc., 3552 (1959).

⁵⁵Behnke, G.T., and Nakamoto, K., Inorg. Chem., 6, 433 (1967).

From the experimental data observed for the chloro complexes it seems that the positions of the chromium-oxygen band and the chromium-chlorine band is significantly different for the tetrachloro and pentachloro oxochromium(V) species. A full discussion of this matter will be undertaken at a later point.

2. Electronic Spectra

For the compounds prepared, the spectra were recorded in mulls at liquid nitrogen temperature and in some cases at room temperature. The solution spectra were recorded using methylene chloride and acetonitrile as solvents. The frequencies of the absorption bands are shown in Table V. Extinction coefficients are listed in the table for the solution spectra. Finally, typical spectra of the compounds are shown in Figures 3-10.

3. Equivalent Conductance

The theory of conductance is treated in many physical and analytical chemistry textbooks⁵⁶ and therefore only a brief description will be presented here. The standard unit of conductance is specific conductance, k , and is defined as the reciprocal of the resistance in ohms of a one centimeter cube of liquid at a specified temperature. The observed conductance of a solution depends inversely on the distance, d , between the electrodes and directly on the surface

⁵⁶Willard, H.H., Merritt, L.L., and Dean, J.A., "Instrumental Methods of Analysis", D. Van Nostrand Co., Inc., 4th Edition, 1965.

TABLE V

ELECTRONIC SPECTRAL BANDS OF Cr(V) COMPLEXES^(a)

Acetonitrile	Methylene Chloride	Mull at R.T.	Mull at 77°A
[Rb₂CrOCl₅]			
			11.95
			12.88
			13.60
			14.55
			15.02
			17.30(sh)
			21.45
			24.20
[Cs₂CrOCl₅]			
			10.84
12.45(19)			11.64
			12.38
18.03(76)			18.53
22.80(sh)			
25.25			
26.15			
26.95			
27.65(7550)			
28.50			
29.20			
40.40(14,500)			
[Me₄NCrOCl₄]			
			11.88
12.84			12.53
			13.23
18.00			18.86
			22.45
25.22			
26.05			

Table V (Continued)

Acetonitrile	Methylene Chloride	Mull at R.T.	Mull at 77°A
26.85			
27.65			
28.45			
29.27			
43.20			
[Et ₄ NCrOCl ₄]			
			12.43
12.50(17)	13.14		13.28
			13.98
			14.72
17.94(99)	18.07		18.30
			22.10
24.40	24.90		
25.00(400)			
25.50			
26.00			
26.70			
27.30			
42.10(sh)	41.80		
45.50(6380)			
[Pr ₄ NCrOCl ₄]			
			11.50
12.48(17)			12.05
			12.65
			12.97
			13.30
			17.24(sh)
17.90(40)			18.30
			22.70

Table V (Continued)

Acetonitrile	Methylene Chloride	Mull at R.T.	Mull at 77°A
25.05(1475)			
25.95			
26.90			
27.70			
28.55			
40.00(990)			
[(C ₆ H ₅) ₄ AsCrOCl ₄]			
12.44(21)		13.54	12.98 13.80 14.44
17.95(80)		18.15	18.35
23.05(sh)		23.20	23.15
25.02(770)			
25.90			
26.87			
27.60			
28.50			
37.05			
37.85(4740)			
38.90			
39.90			
[Bu ₄ P ₄ CrOCl ₄]			
12.66(15)	13.50(21)	12.67	11.44 12.35 13.22 15.00 16.00 16.82

Table V (Continued)

Acetonitrile	Methylene Chloride	Mull at R.T.	Mull at 77°A
18.03(77)	18.15(148)	18.05	18.20
22.64(362)	22.90(sh)	22.22	22.50
	25.10(1780)		
	26.05		
	26.75		
	27.55		
	32.25(2015)		
$[(C_6H_5CH_2)(C_6H_5)_3PCrOCl_4]$			
12.48(16)	13.33(10)	12.40	11.98 12.72 13.70
18.02(74)	18.11(119)	17.90	17.90
23.10(sh)	22.75(1510)	21.70	22.20
25.30	25.12(2185)		
26.13	25.95		
26.92	26.72		
27.67(910)	27.52		
28.45	28.22		
29.33			
36.75	36.50(3700)		
37.55(5000)	37.60(5151)		
38.50	38.50(5150)		
$[(Et_4N)_2CrOF_5]$			
			8.29 8.41
14.15			
14.85	16.53(0.8)		14.87
15.63(0.8)			15.52

Table V (Continued)

Acetonitrile	Methylene Chloride	Mull at R.T.	Mull at 77°A
22.20(18.5)	22.15(16.5)	.	22.33
22.70(18.5)			25.50
27.30			26.10
28.00			27.00
28.58			27.75
29.40(86)	29.12(105)		28.55
30.07			29.40
30.82			30.20
31.50			31.10
	35.82(sh)		
36.90(118)	36.60(446)		36.80(sh)
38.60	39.45(324)		
39.65			
40.70			
41.70			
 $\text{Cs}_2\text{CrO}(\text{tart})\text{Cl}_3$			
			10.73
			11.68
		14.04	14.38
			15.37
		20.18	20.45
		23.00	22.95
		29.70	29.30
 $\text{Cs}_2\text{CrO}(\text{C}_3\text{H}_2\text{O}_5)\text{Cl}_3$			
			10.88
			11.63
			12.43
			14.33

Table V (Continued)

Acetonitrile	Methylene Chloride	Mull at R.T.	Mull at 77°A
			14.92
			21.05(sh)
			23.00
			23.45(sh)
			29.05
$\text{Cs}_2\text{CrO}(\text{C}_4\text{H}_4\text{O}_5)\text{Cl}_3$			10.88
			11.74
			14.13
			15.25
			20.20
			23.85
			23.35(sh)
			28.32(sh)
			29.25
			29.95(sh)

^aNumbers in parenthesis are extinction coefficients.

Figure 3. Electronic Spectrum of $(C_6H_5)_4AsCrOCl_4$ in Nujol at Room Temperature.

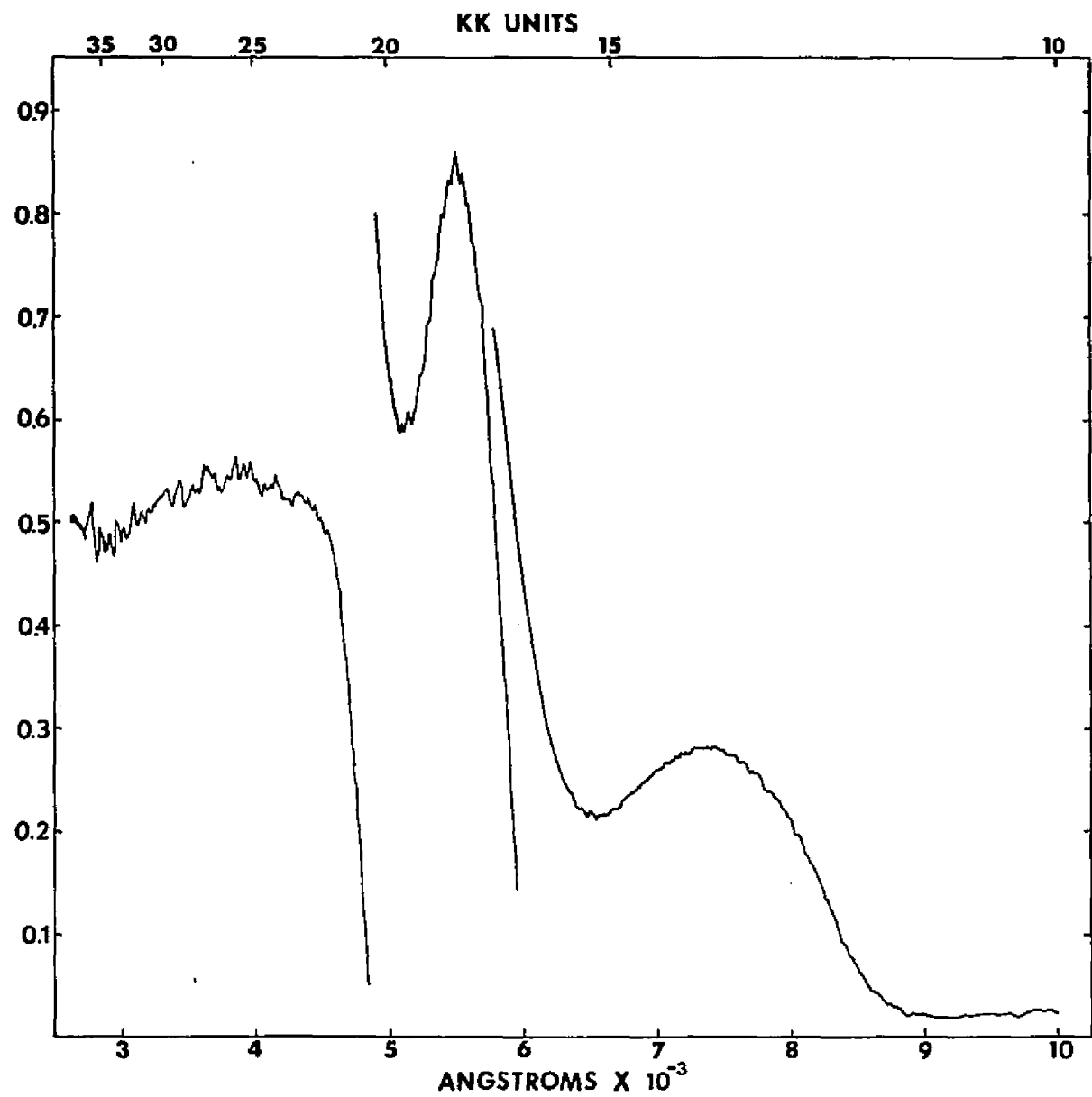


Figure 4. Electronic Spectrum of $(C_6H_5)_4AsCrOCl_4$ in Nujol at $77^\circ A$.

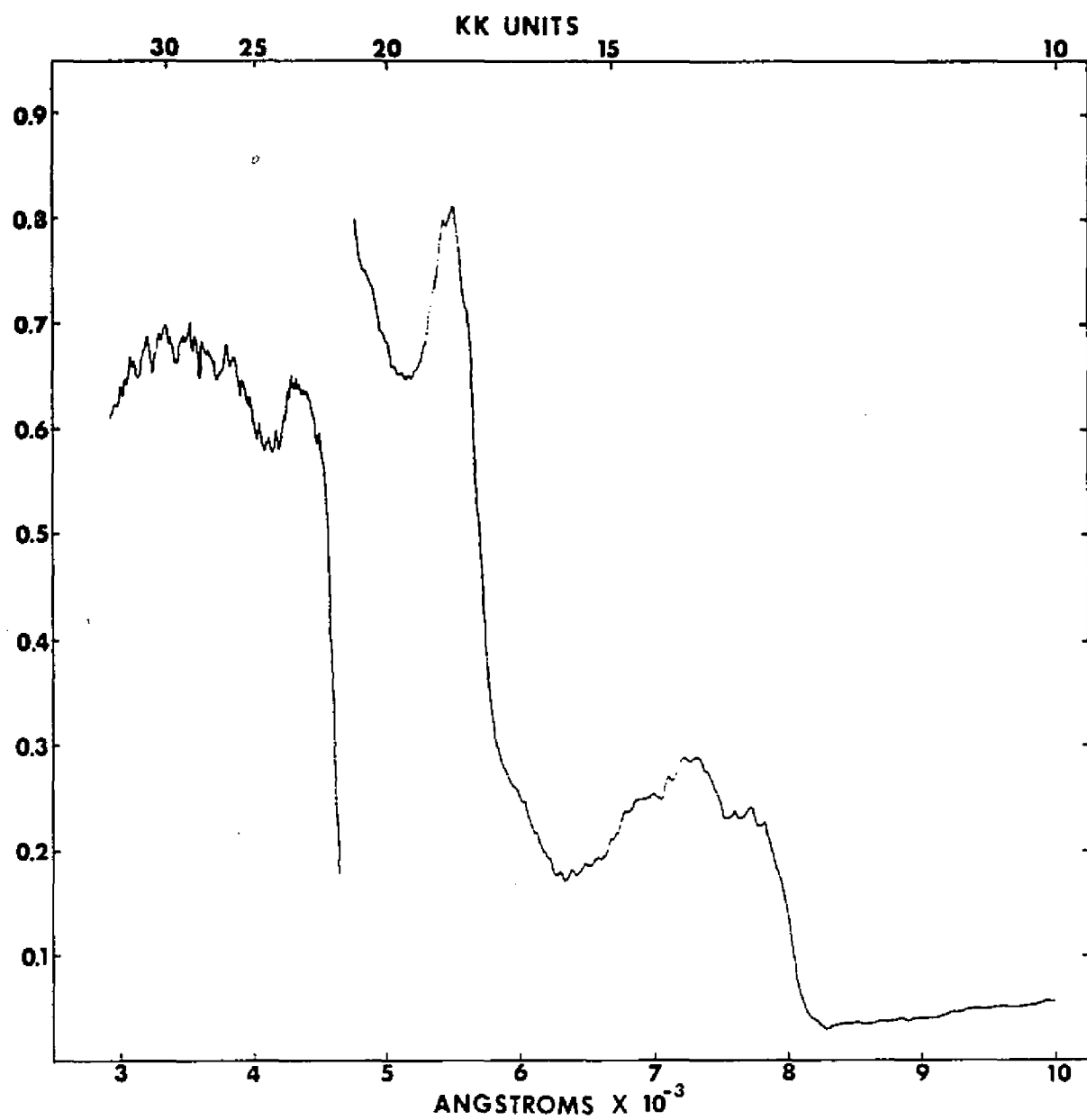


Figure 5. Electronic Spectrum of $\text{Cs}_2\text{CrOCl}_5$ in Nujol at 77°A .

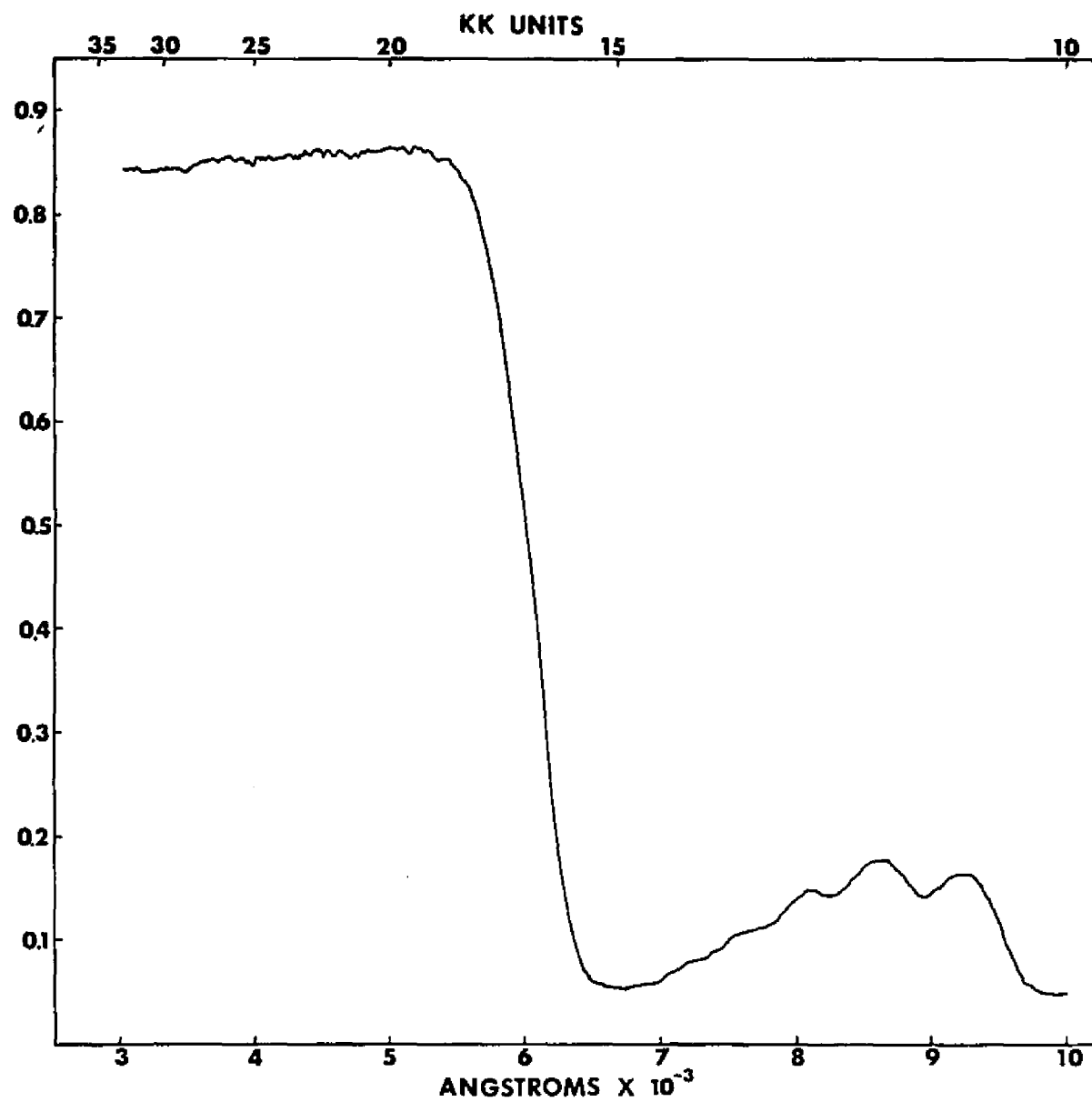


Figure 6. Electronic Spectrum of $(C_6H_5)_4AsCrOCl_4$ in Acetonitrile.

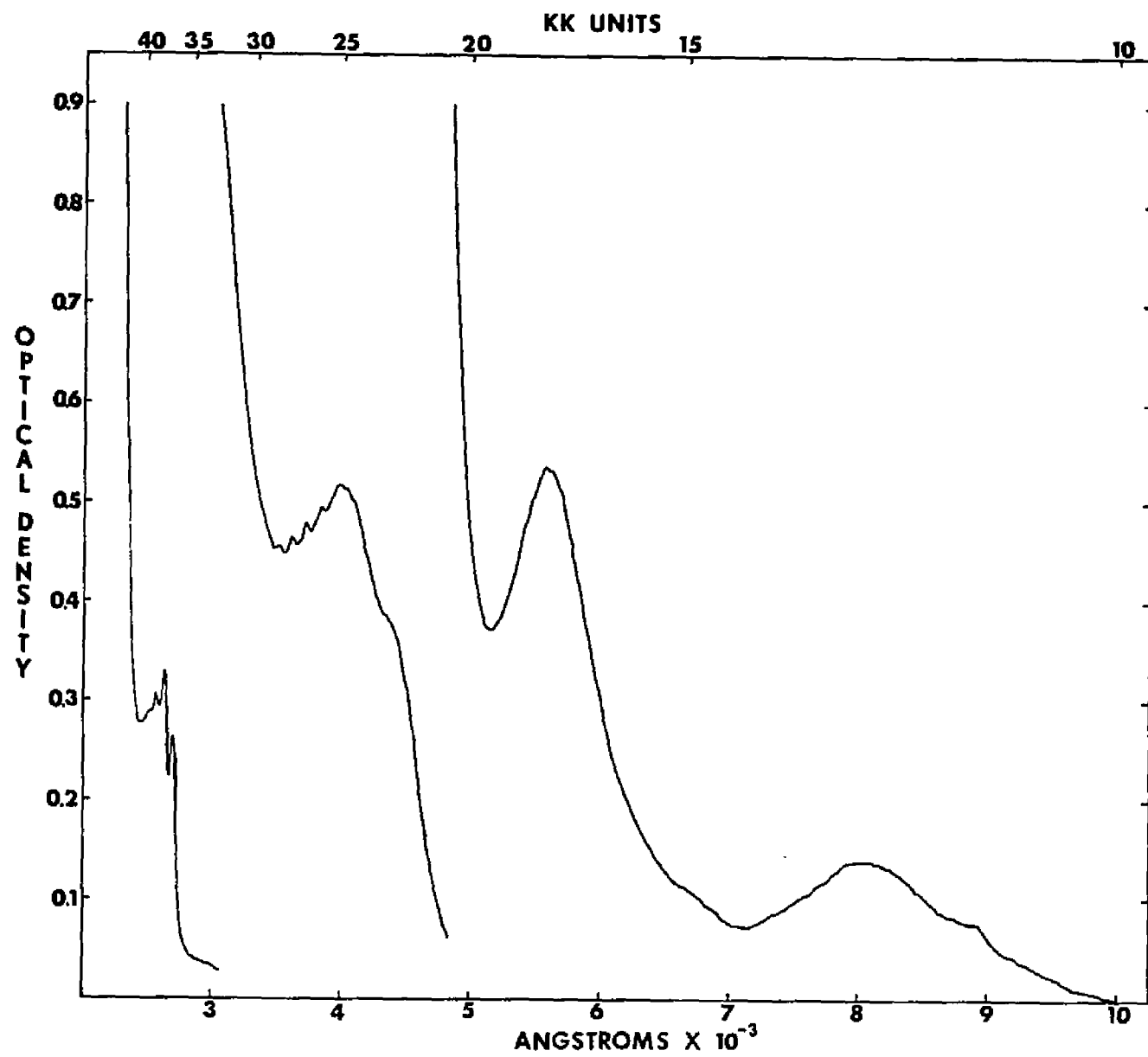


Figure 7. Electronic Spectrum of $\text{Cs}_2\text{CrOCl}_5$ in Acetonitrile.

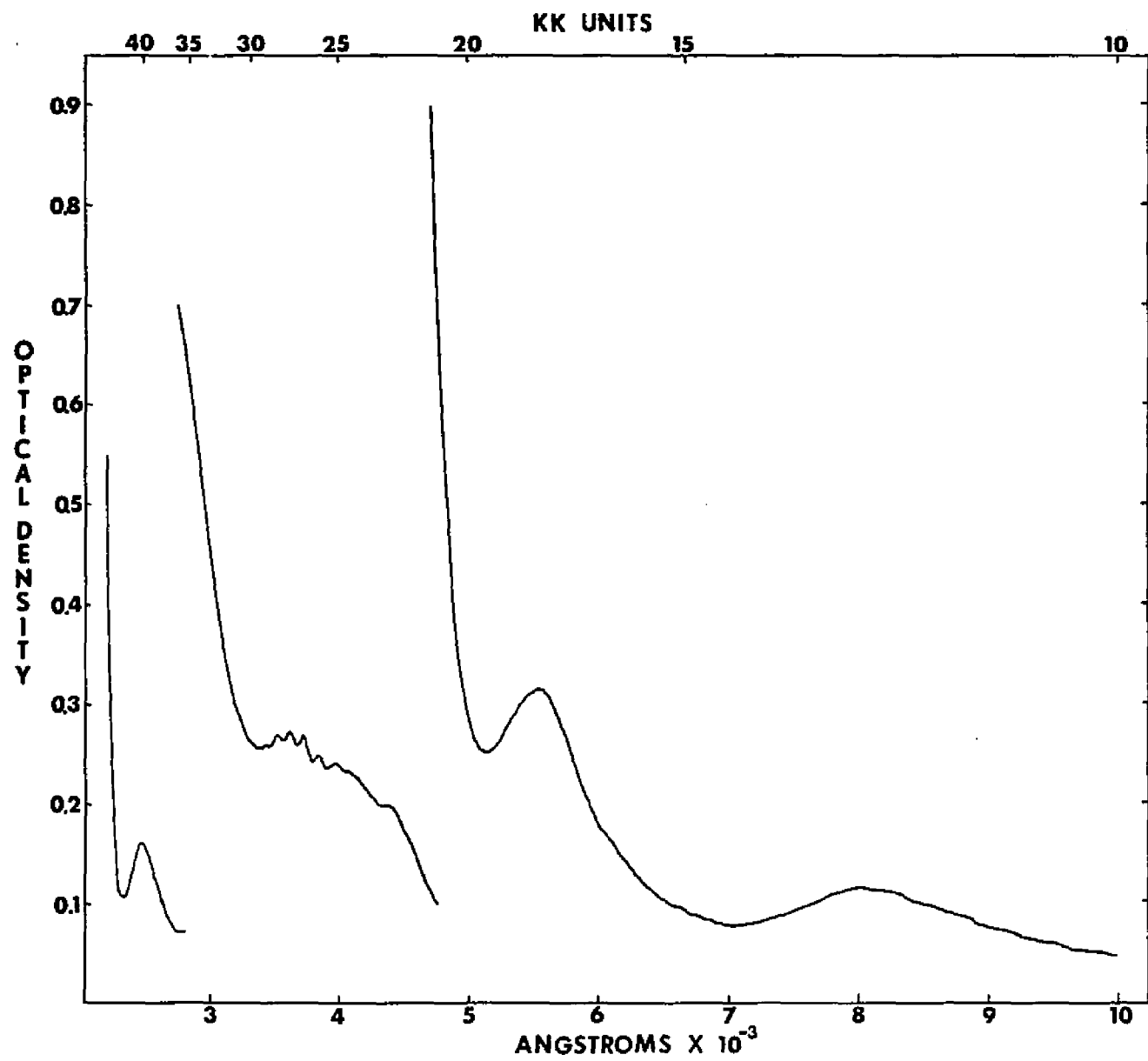


Figure 8. Electronic Spectrum of $(\text{C}_6\text{H}_5\text{CH}_2)(\text{C}_6\text{H}_5)_3\text{PCrOCl}_4$ in Methylene Chloride.

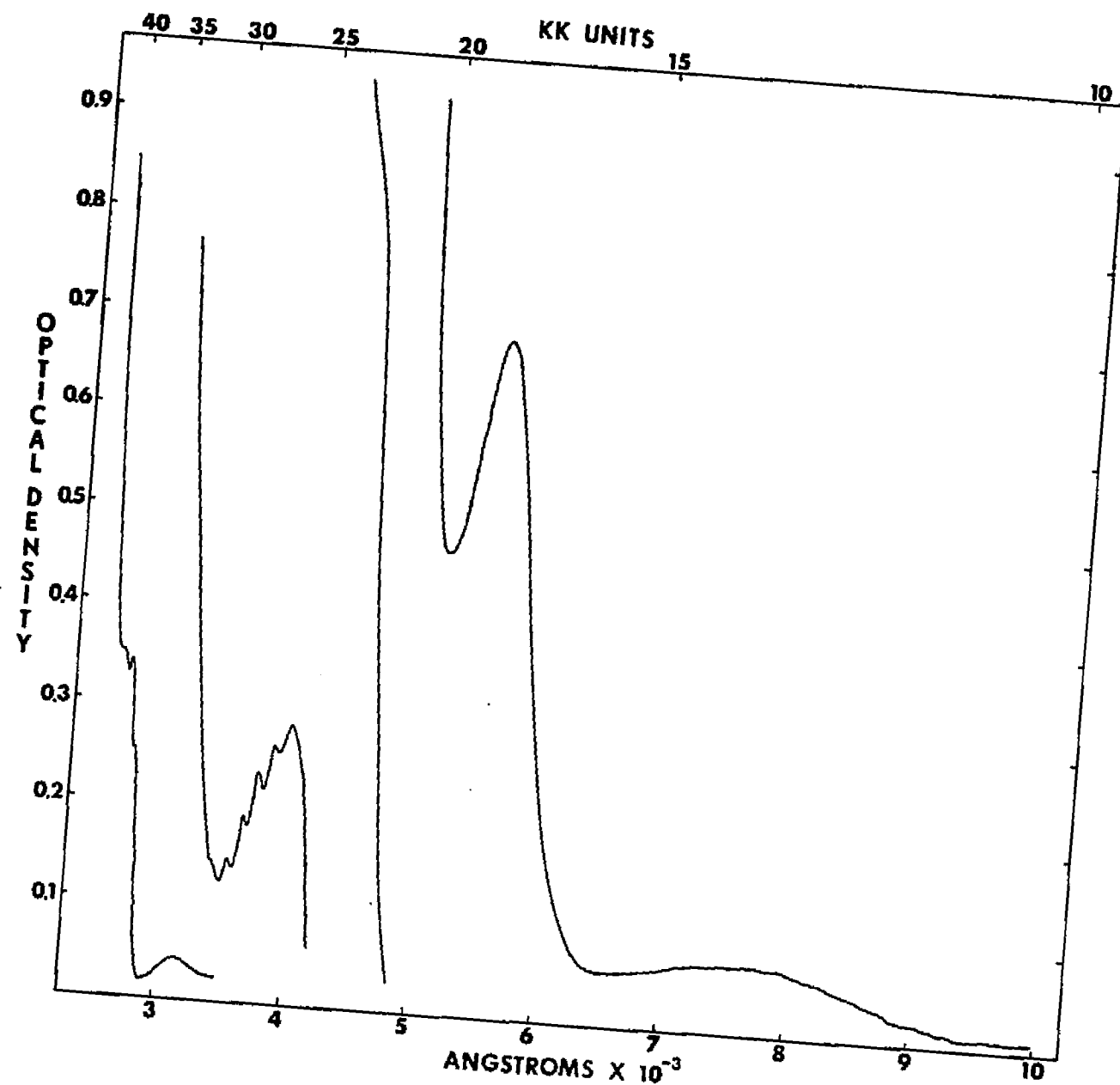


Figure 9. Electronic Spectrum of $\text{Cs}_2\text{CrO}(\text{tart})\text{Cl}_3$ in Nujol at 77°A .

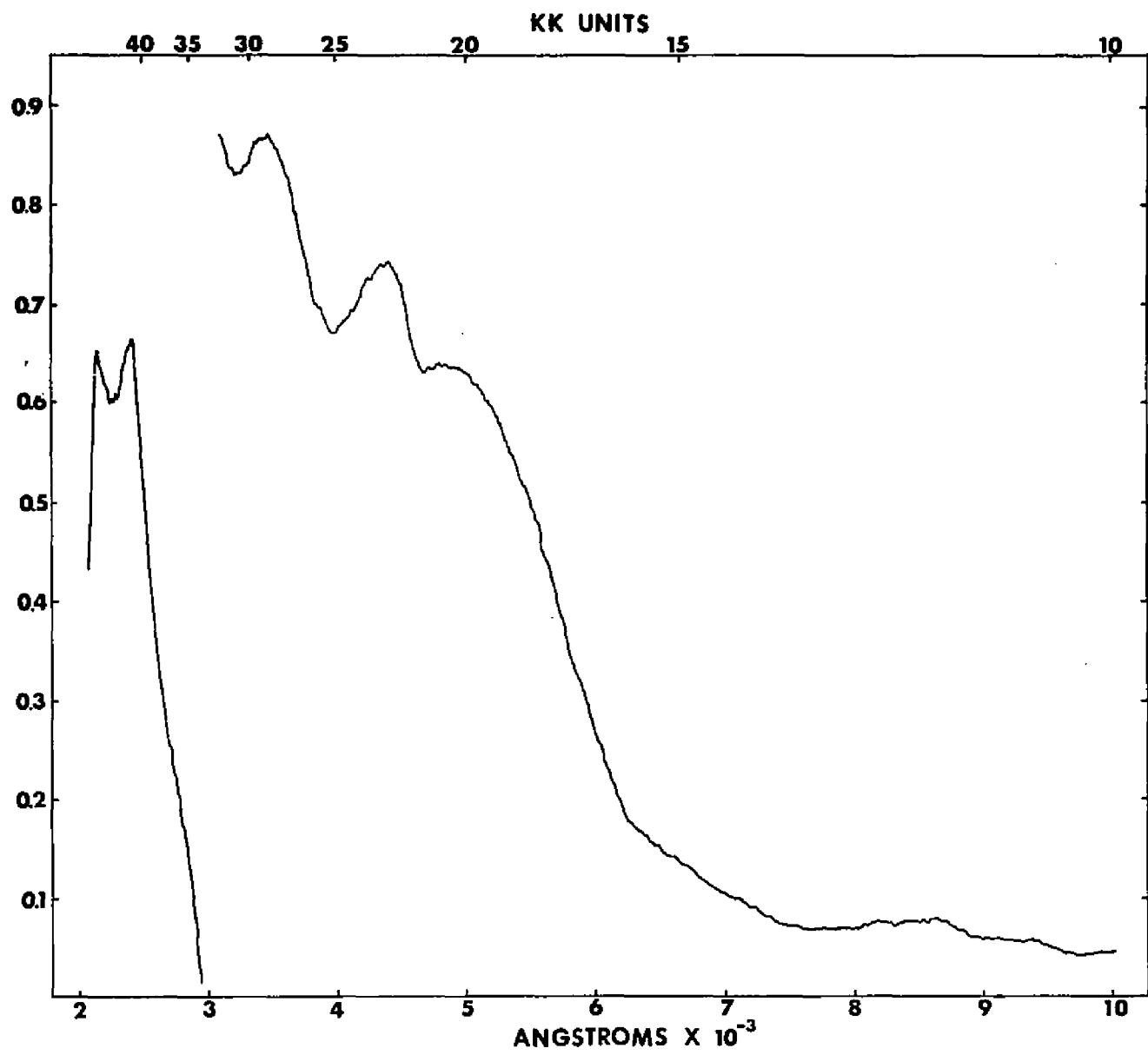
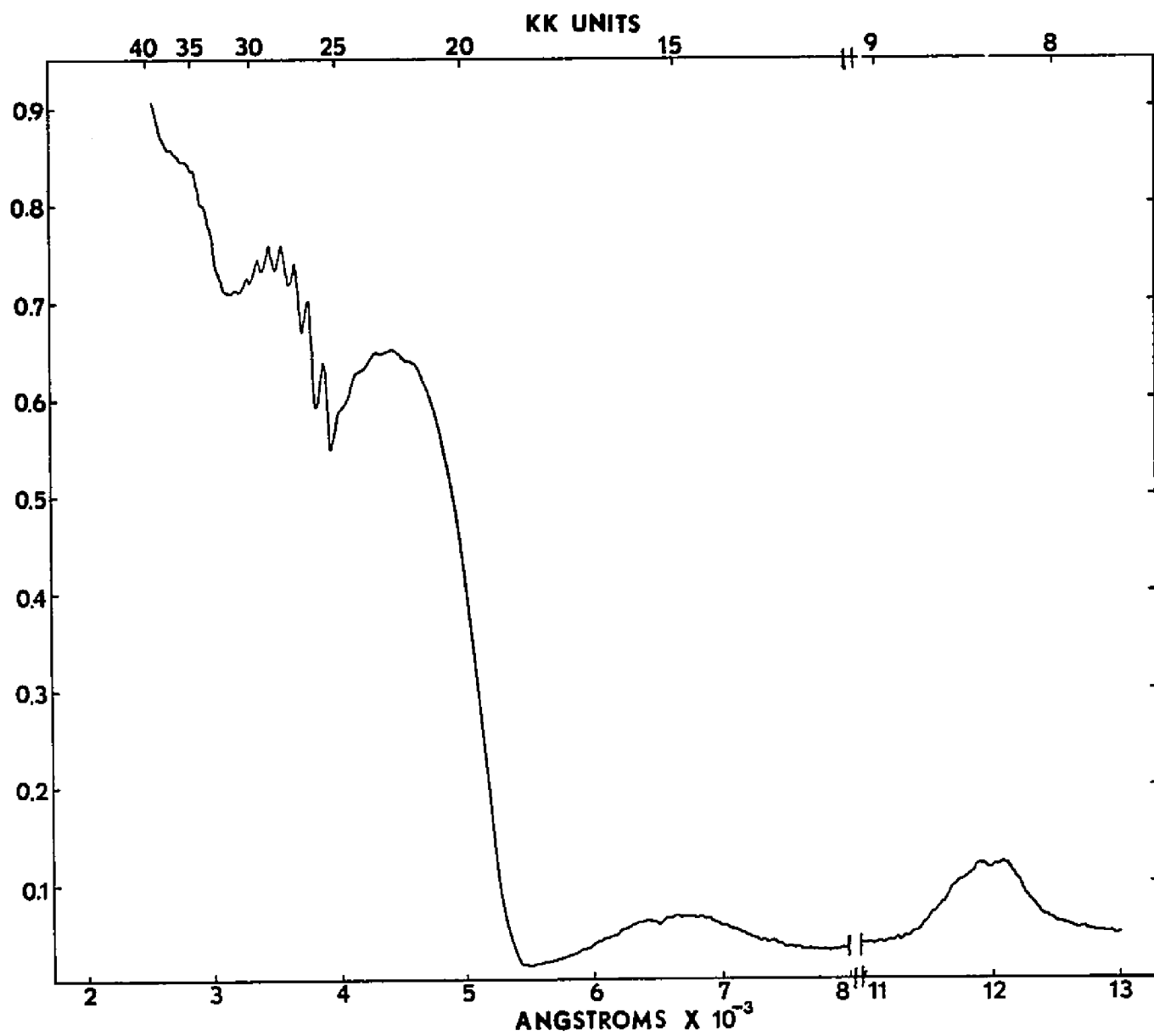


Figure 10. Electronic Spectrum of $(Et_4N)_2CrOF_5$ in Nujol at $77^\circ K$.



surface area, A , of the electrodes. This relationship is expressed in the following formula:

$$1/R = k \frac{A}{d} \quad \dots 7$$

However, in order to express the ability of individual ions to conduct, chemists employ a function termed equivalent conductance. The relationship between equivalent conductance and specific conductance is:

$$\Lambda = 1000 \frac{k}{C} \quad \dots 8$$

where Λ represents the equivalent conductance and C represents the concentration of the solution in gram-equivalents/liter. Substituting the value for k from eq.7 into eq.8 gives the following expression.

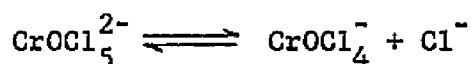
$$\Lambda = \frac{1000d}{R A C} \quad \dots 9$$

The value, d/A , represents what is termed the cell constant and can be determined by measuring the resistance of a solution of known conductance. By knowing the resistance, concentration, and equivalent conductance, one can then calculate the cell constant. Likewise one can calculate the cell constant directly by measuring the dimensions of the electrodes and the distance between them. The conductivity cell used in these determinations was equipped with two platinum electrodes and had a volume of approximately 15 ml.

Results of the measurements performed are listed in Table VI. These values may be compared with those listed by Drago

and Purcell⁵⁷ for a number of one to one electrolytes. The range of equivalent conductance for these known compounds was 168 to 208 ohm⁻¹ cm². From the data in Table VI it would appear that the species containing CrOCl_4^- are one to one electrolytes.

Nelson, Nathan, and Ragsdale⁵⁸ reported conductivity data obtained in acetonitrile for a series of complexes of the type $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{L} \cdot x\text{H}_2\text{O}$, where L represents a 4-substituted quinoline-1-oxide. The range of the conductance data for this series of complexes was 198 - 296 cm² ohm⁻¹ which they indicated was in the range for 2:1 electrolytes. Therefore, it appears that the conductivity of the $\text{Cs}_2\text{CrOCl}_5^-$ complex is much greater than that for a two to one electrolyte which would indicate some further dissociation of the CrOCl_5^{2-} species. Therefore, from the conductivity data it is highly possible that in solution RCrOCl_4^- and $\text{R}_2\text{CrOCl}_5^-$ are present in the same form. This could easily result if CrOCl_5^{2-} species dissociate according to the following equation:



The resulting solution would then contain a mixture of CrOCl_4^- and CrOCl_5^{2-} .

⁵⁷Drago, R.S., and Purcell, K.F., "Coordinating Solvents", in "Non-Aqueous Solvent Systems", T.C. Waddington (ed.), Academic Press, 1965, pp.211-251.

⁵⁸Nelson, J.H., Nathan, L.C., and Ragsdale, R.O., Inorg. Chem., 7, 1840 (1968).

TABLE VI
EQUIVALENT CONDUCTANCE OF OXOCHROMIUM(V) CHLORO COMPLEXES
IN ACETONITRILE

Compound	Equivalent Conductance
$\text{Me}_4\text{NCrOCl}_4$	$177 \text{ ohm}^{-1} \text{ cm}^2$
$\text{Et}_4\text{NCrOCl}_4$	162
$\text{Pr}_4\text{NCrOCl}_4$	163
$\text{Cs}_2\text{CrOCl}_5$	354

4. Magnetic Susceptibility

a. Gouy Method: The Gouy method for measuring magnetic susceptibility is discussed in detail in a number of texts^{59,60}. Therefore, only a brief outline will be presented here.

The experimental determination of the magnetic moment involves the measurement of the magnetic susceptibility and from this one can calculate the magnetic moment. To measure the magnetic susceptibility, the sample is packed in a cylindrical tube of uniform cross-section and suspended in a magnetic field such that one end of the sample is at the high intensity point of the field, H (center of the pole cap), while the other end of the sample projects above the magnetic poles to where the field, H_0 , is almost negligible. The force acting on the sample is given by equation 10

$$F = \frac{1}{2}A(H^2 - H_0^2)(K - K') + S \quad \dots 10$$

where A = cross sectional area of sample

K = magnetic susceptibility of sample per unit of volume

K' = magnetic susceptibility of the atmosphere per unit of volume

S = force due to sample tube alone.

⁵⁹Selwood, P.M., "Magneto Chemistry", Interscience Publishers, Inc., Second Edition, 1956.

⁶⁰Figgis, B.N. and Lewis, J., in J. Lewis and R.G. Wilkins "Modern Coordination Chemistry", Interscience Publishers, Inc., 1960.

The cross sectional area of the sample is assumed to be uniform and, hence, the factor $\frac{1}{2}A(H^2 - H_0^2)$ may be treated as a constant. The volume susceptibility can be related to the mass susceptibility, χ_g , by the equation $\chi_g = K/d$ where d = density. Assuming that K' falls within the limits of accuracy of the measurements which it does for most measuring equipment, equation 10 then becomes

$$10^6 \chi_g = \beta \frac{F'}{w} \quad \dots 11$$

where χ_g = gram susceptibility of the sample

β = tube calibration constant

w = weight of the sample in grams

$F' = (F - S)$ (force exerted on the sample in mg.).

The tube calibration constant can be determined by measuring F' on a sample whose gram susceptibility is reported in the literature such as $\text{Co}[\text{Hg}(\text{SCN})_4]$ or $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and then using equation 11 to calculate β .

The molar susceptibility, χ_M , is calculated by multiplying χ_g by the molecular weight of the compound. The molar susceptibility must be corrected for the diamagnetism of the substance using the values of Pascal's constants from Selwood⁵⁹. This correction is subtracted from the molar susceptibility to obtain the actual susceptibility, $\chi_M^{\text{Corr.}}$. $\chi_M^{\text{Corr.}}$ is related to the magnetic moment, μ , according to equation 12 from which μ can then be calculated.

$$\mu = 2.84(\chi_M^{\text{Corr.}} \times T)^{\frac{1}{2}} \quad \dots 12$$

b. NMR Method: A method to measure the magnetic susceptibility of a paramagnetic ion of low concentration in solution was demonstrated by Evans⁶¹. The greatest advantage of this method is that a much smaller sample is required than with the Gouy method and the accuracy is comparable with that of the Gouy method. This method employs the use of proton NMR spectra. It is based on the principle that the position of a given proton resonance in the spectrum of a molecule is dependent on the bulk susceptibility of the medium in which the molecule is found. The shift of a proton resonance line of an inert substance due to the presence of paramagnetic ions is given by equation 13

$$\frac{\delta\nu}{\nu_0} = \frac{2\pi}{3}(\chi_v - \chi'_v) \quad \dots 13$$

where $\delta\nu$ = shift of resonance line

ν_0 = applied magnetic field

χ_v = volume susceptibility of the solution containing paramagnetic ions

χ'_v = volume susceptibility of a reference solution.

The mass susceptibility, χ_g , of the dissolved sample is given by equation 14

$$\chi_g = \frac{3\delta\nu}{2\pi\nu_0 m} + \chi_o + \chi_o \frac{(d_o - d_s)}{m} \quad \dots 14$$

where $\delta\nu$ = frequency separation between the two lines in cps

ν_0 = frequency at which the proton resonances are being studied in cps

⁶¹Evans, D.F., J. Chem. Soc., 2003 (1959).

χ_o = mass susceptibility of the solvent

d_o = density of the solvent

d_s = density of solution

After calculating the gram susceptibility from equation 14 one can determine the magnetic moment by the same method indicated previously.

In Table VII are recorded the magnetic susceptibilities of the complexes prepared. It can be noted that all the values obtained compare well with the spin-only value for one unpaired electron which is indicative of a Cr(V) species, except the hydroxyl acid complexes. Figure 11 is an example of the type of splitting observed in the magnetic susceptibility determination by the NMR method.

5. Electron Spin Resonance Spectra

Electron spin resonance spectroscopy presents a powerful tool for the study of chemical species with unpaired electrons. It provides information on the number of unpaired electrons and also on the distribution of the electrons in the molecule. A brief description of the theoretical aspects of ESR spectroscopy will be presented here. For a more thorough discussion of ESR principles the reader may refer to references 62-64.

For an electron with spin $s = \frac{1}{2}$, the spin angular momentum

⁶²Bersohn, M., and Baird, J.C., "Electron Paramagnetic Resonance", W.A. Benjamin, Inc., New York, N.Y., 1966.

⁶³Carrington, A., and McLachlan, A.D., "Introduction to Magnetic Resonance", Harper and Row Publishers, New York, N.Y., 1967.

⁶⁴Pake, G.E., "Paramagnetic Resonance", W.A. Benjamin, Inc., New York, N.Y., 1962.

TABLE VII
MAGNETIC MOMENTS OF THE OXOCHROMIUM COMPLEXES

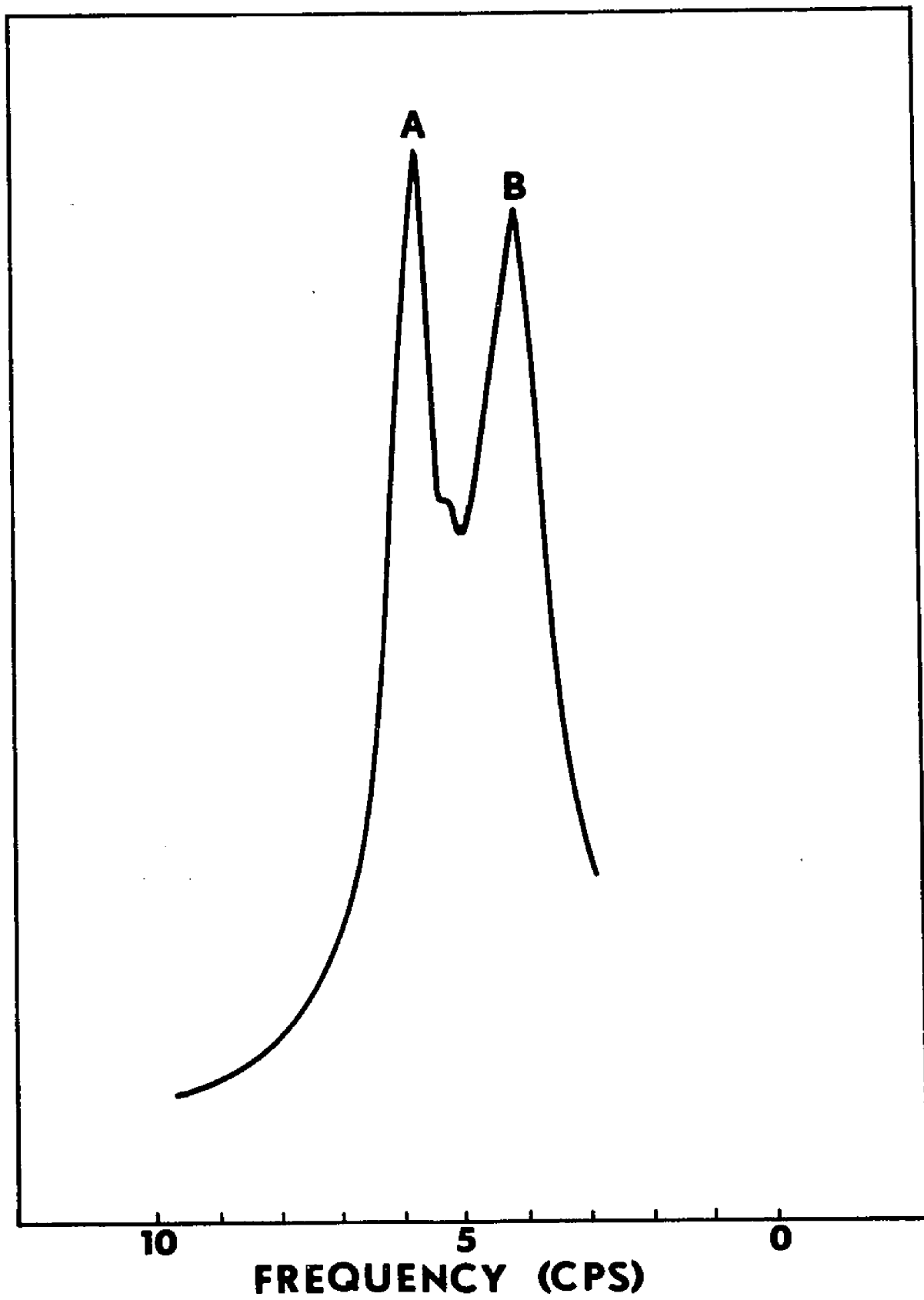
Compound	Gouy Method ^(a)	NMR Method ^(b)
Rb ₂ CrOCl ₅	1.92	----
Cs ₂ CrOCl ₅	1.85 ^(c)	----
Me ₄ NCrOCl ₄	1.79	----
Et ₄ NCrOCl ₄	1.78	1.64
Pr ₄ NCrOCl ₄	1.74	1.77
Bu ₄ PCrOCl ₄	----	1.74
(C ₆ H ₅) ₄ AsCrOCl ₄	1.87	1.96
(C ₆ H ₅ CH ₂)(C ₆ H ₅) ₃ PCrOCl ₄	----	1.73
(Et ₄ N) ₂ CrOF ₅	----	1.52
Cs ₂ CrO(tart)Cl ₃	2.78	----
Cs ₂ CrO(C ₃ H ₂ O ₅)Cl ₃	2.99	----
Cs ₂ CrO(C ₄ H ₄ O ₅)Cl ₃	3.06	----

^aUnits are in Bohr Magnetons.

^bSolvent used was CH₂Cl₂.

^cBrown³⁷ reported 1.80 for this compound.

Figure 11. The proton NMR spectrum in CH_2Cl_2 in a coaxial set of tubes containing CH_2Cl_2 in the inner tube (peak A) and a solution of $\text{Et}_4\text{N}[\text{CrOCl}_4]$ in CH_2Cl_2 in the annulus (peak B).



quantum number can have the values of $m_s = \pm \frac{1}{2}$. These values are doubly degenerate in the absence of an applied magnetic field. If the electron is placed in a magnetic field the energy is given by the equation:

$$E = -\mu H \cos\theta \quad \dots 15$$

where E is the energy in ergs, μ is the magnetic dipole moment in ergs per gauss, H is the magnetic field strength in gauss and θ is the angle between the magnetic moment and the direction of the external field. Non-degenerate energy levels can be produced from the interaction of the magnetic moment of the electron with an applied magnetic field. The low energy state has its spin magnetic moment aligned with the field while the higher energy state has its spin magnetic moment opposed to the field. A transition between the two different energy states occurs by the absorption of radiation in the microwave region of the electromagnetic spectrum when the magnetic field is of the order of several thousand gauss. The energy transition is given by equation 16:

$$E = h\nu = g\beta H \quad \dots 16$$

where h = Planck's constant

ν = frequency of radiation

g = Landé' splitting factor

β = Bohr Magneton

H_0 = magnetic field strength.

Paired electrons do not give rise to an ESR signal due to the fact that if one of the electrons undergoes a flip both electrons will possess the same set of quantum numbers. This is forbidden by the Pauli exclusion principle.

Only electromagnetic waves of frequency $\nu = g\beta H_0/h$ have exactly the right amount of energy to provide the difference of energy between the two states. The coincidence of the energy of the quantum, $h\nu$, and the energy difference between the levels $m_s = \frac{1}{2}$, is called resonance. Both the field and the frequency must be adjusted from one sample to another so that neither one alone is adequate to specify the position of a given absorption. Therefore the Landé splitting factor, g , is used. The g value is the ratio of the magnetic moment of the electron to the total angular momentum of the electron. This factor equals 2.002322 for an unbound electron but when the electron is in the orbitals of an atomic nucleus the value may be appreciably altered. The g value can differ from the free-electron value because of spin-orbit coupling which places a small orbital angular momentum on the unpaired electron and alters its effective magnetic moment. In general, the magnitude of g depends upon the orientation of the molecule containing the unpaired electron with respect to the magnetic field. In a solution or in the gas phase, g is averaged over all orientations because of the free motion of the molecules but in a crystal, movement is restricted. When the paramagnetic species is located in a perfectly cubic crystal site the g value is independent of the orientation of the

crystal and is said to be isotropic. In a crystal site of lower symmetry the g value depends upon the orientation of the crystal and is said to be anisotropic. The g_z or $g_{||}$ value is the g value obtained when the z axis is parallel with the external magnetic field. The g values along the x and y axis are g_x and g_y , which in a tetragonal site are equal and referred to as g_{\perp} , is the g value obtained with the external magnetic field perpendicular to the z axis. The $g_{||}$ and g_{\perp} values are related to g average by equation 17.

$$g^2 = 1/3g_{||}^2 + 2/3g_{\perp}^2 \quad \dots 17$$

Up to this point we have considered only the interaction of an electron spin with an external magnetic field. Another aspect which is of great interest to the chemist is the further interaction between the electron spin and the internal magnetic fields, particularly those due to the magnetism of nuclei in the same molecule. The magnetic interactions between the electron spin and nuclear spin cause the ESR spectrum to consist of a number of lines rather than a single line. The resulting group of lines in the ESR spectrum is termed the hyperfine structure of the spectrum and is caused by the hyperfine interaction of the nucleus and the electron. The further splitting of the electron states results from the presence of the magnetic field caused by the presence of the nuclear moment. When an unpaired electron comes in the vicinity of a nucleus with a spin, I , an interaction takes place which causes the absorption signal to be split into $2I + 1$ components.

Since about 90% of the chromium nuclei have zero spin ($^{50,52,54}\text{Cr}$) these nuclei have no magnetic moment and hence no hyperfine splitting occurs for these nuclei. However, ^{53}Cr , whose natural abundance is 9.55%, has a nuclear spin of $3/2$ and hyperfine interaction between this nucleus and the unpaired electron is to be expected. The resulting energy level diagram is shown in Figure 12. The energies of each sublevel is given by the equation:

$$E(M_s, M_I) = g\beta H_0 M_s + A M_s M_I$$

where A is the electron spin-nuclear spin coupling constant and M_I is the nuclear spin quantum number. The allowed transitions are determined by the selection rules $\Delta M_s = \pm 1$ and $\Delta M_I = 0$. Therefore the allowed transitions between the various states, $E_8 - E_1$, $E_7 - E_2$, $E_6 - E_3$, and $E_5 - E_4$ can be calculated:

$$\begin{aligned} E_8 - E_1 &= [g\beta H_0 (+\frac{1}{2}) + A(+\frac{1}{2})(+\frac{3}{2})] - [g\beta H_0 (-\frac{1}{2}) + A(-\frac{1}{2})(+\frac{3}{2})] \\ &= g\beta H_0 + 3/2A \end{aligned}$$

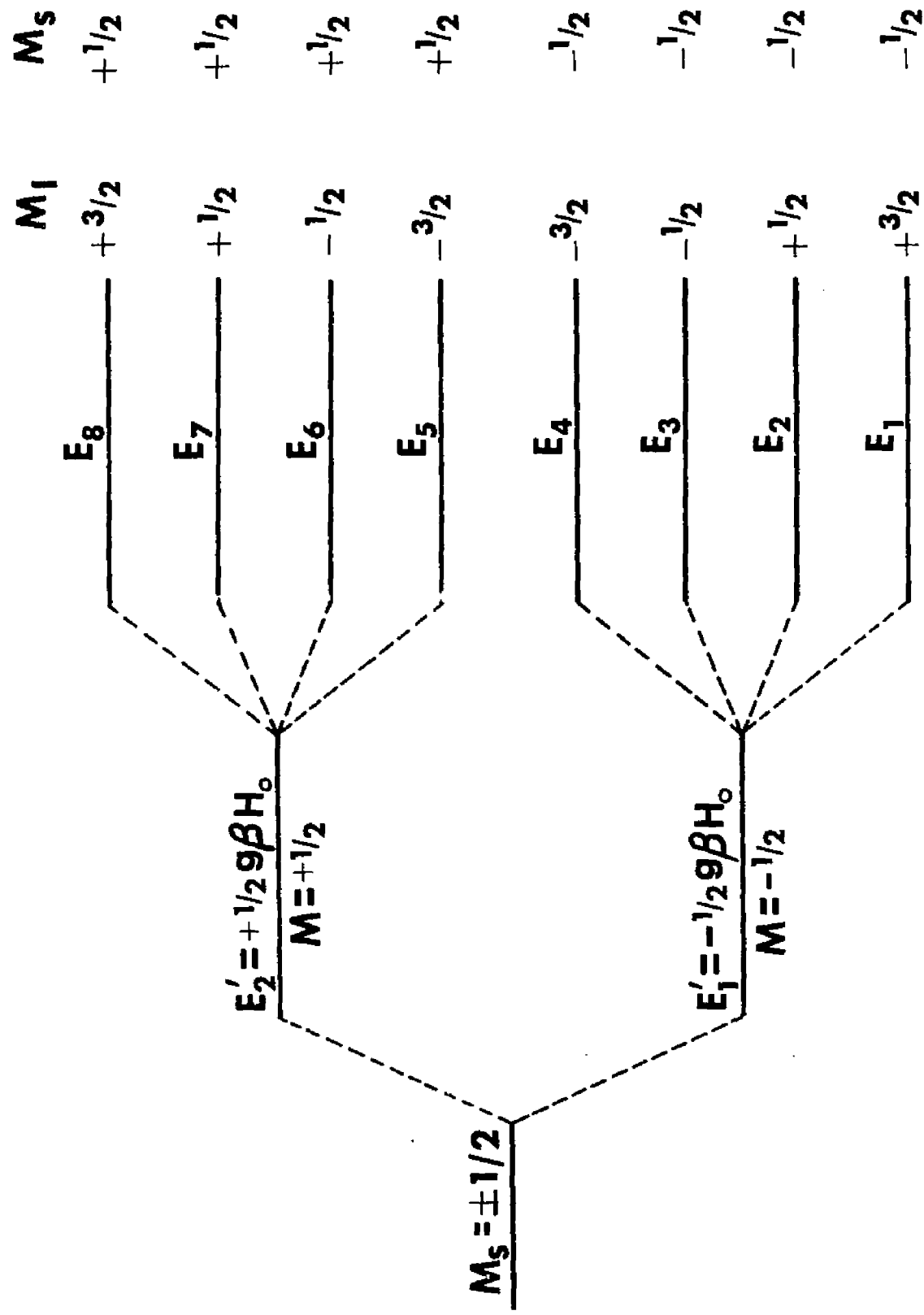
$$E_7 - E_2 = g\beta H_0 + \frac{1}{2}A$$

$$E_6 - E_3 = g\beta H_0 - \frac{1}{2}A$$

$$E_5 - E_4 = g\beta H_0 - 3/2A$$

The above treatment indicates that a single intense absorption should occur due to electrons moving about the Cr(V) nuclei with zero spin corresponding to the $E'_1 \leftarrow E'_2$ transition in the diagram. Four lower intensity bands, two on either side of

Figure 12: Hyperfine splitting of the energy levels of an electron bound to a nucleus having a spin of $3/2$ and in the influence of an external magnetic field. The first column (A) represents the unperturbed energy levels, the second column (B) shows the splitting of this level due to an applied external field and the third column (C) demonstrates the hyperfine splitting of the electronic energy levels because of a nuclear spin of $3/2$.



(A)

(B)

(C)

the $E'_1 \leftarrow E'_2$ transition, should be found due to the interaction between the electrons and chromium nuclei having a spin of $+3/2$. The ESR spectrum of some of the Cr(V) complexes prepared in this study are shown in Figures 13-16. The hyperfine splitting from the ^{53}Cr isotope which is predicted is resolved in only one of the spectra. Presumably this is due to the low percentage of the natural abundance of the ^{53}Cr isotope. The calculated g values are listed in Table VIII.

In the spectra of $(\text{Et}_4\text{N})_2\text{CrOF}_5$ (Figures 15 and 15a) one can observe what appears to be superhyperfine structure. In Figure 15 the very broad bands observed are possibly the hyperfine structure due to the interaction of the unpaired electron with the ^{53}Cr isotope while the much narrower splitting which is much more visible in Figure 15a is probably the superhyperfine structure due to the ^{19}F isotope. The observed splitting in Figure 15a is approximately 18 gauss while Manoharan and Rogers⁴³ observed a 10.5 gauss separation in an HF solution containing a mixture of CrOF_4^- and CrOF_5^{2-} . The ESR signal due to the ^{19}F isotope should be split into five components with intensity ratios of 1:4:6:4:1. In Figure 15a only four lines are observed while the fifth peak may be covered by the strong central signal. It is difficult to determine the intensities but it appears that they could be in the desired ratios. Two, and possibly three, of the peaks due to the ^{19}F superhyperfine structure appear to be split into a doublet with one being slightly more intense than the other. The doublet would be expected due to the

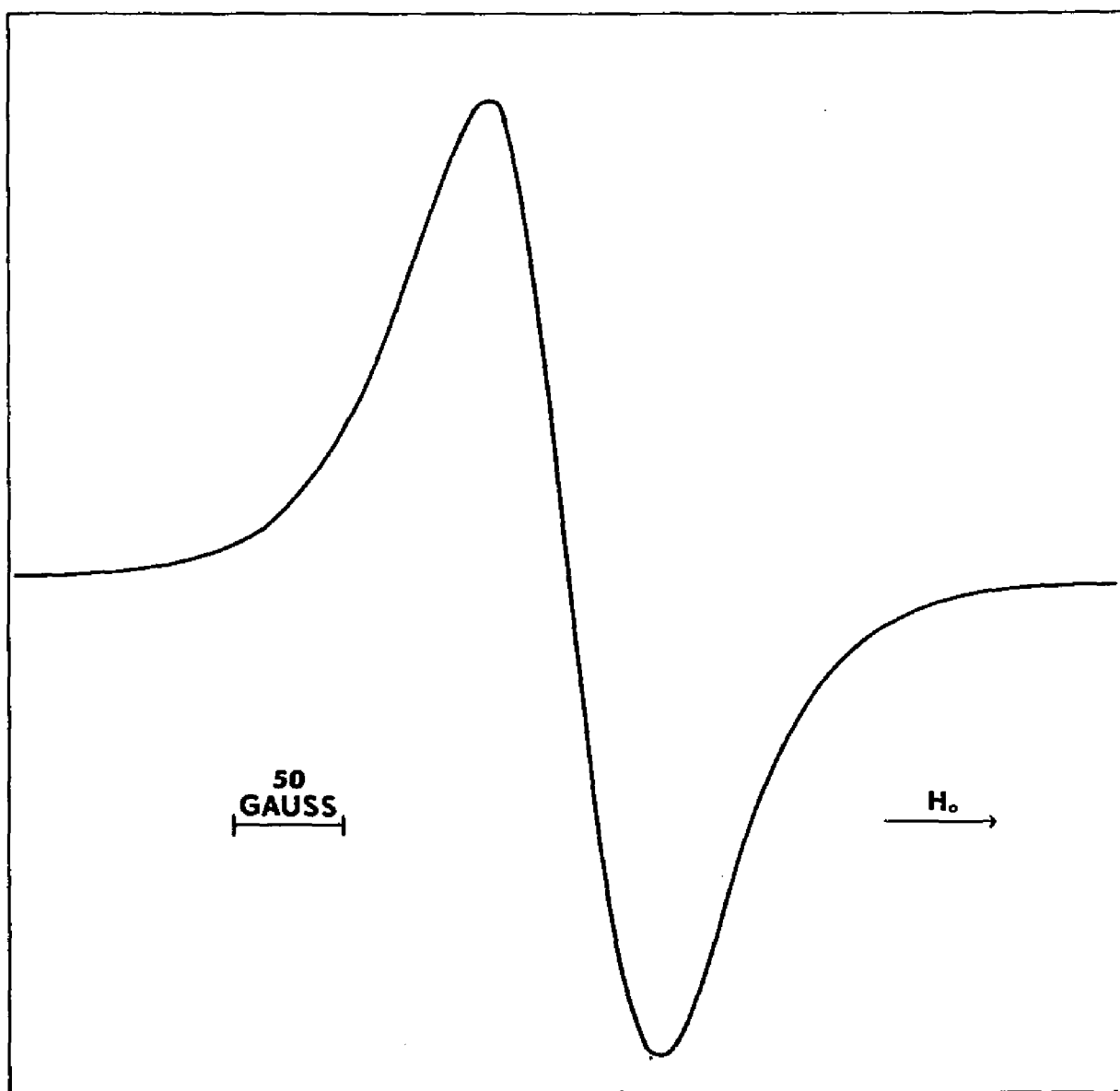


Figure 13. ESR Spectrum of $\text{Bu}_4\text{PCrOCl}_4$ in the Solid State.

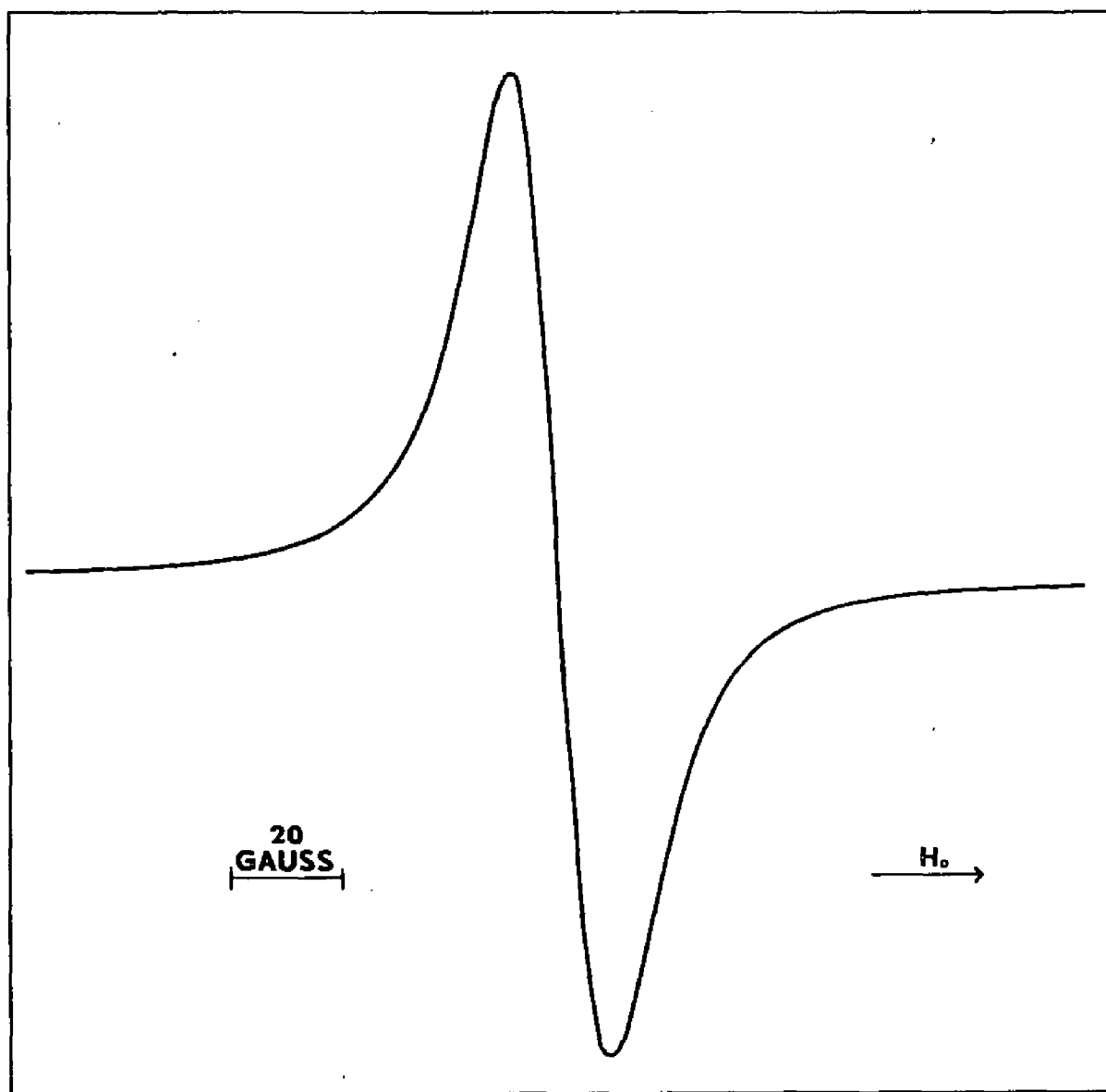


Figure 14. ESR Spectrum of $\text{Rb}_2\text{CrOCl}_5$ in the Solid State.

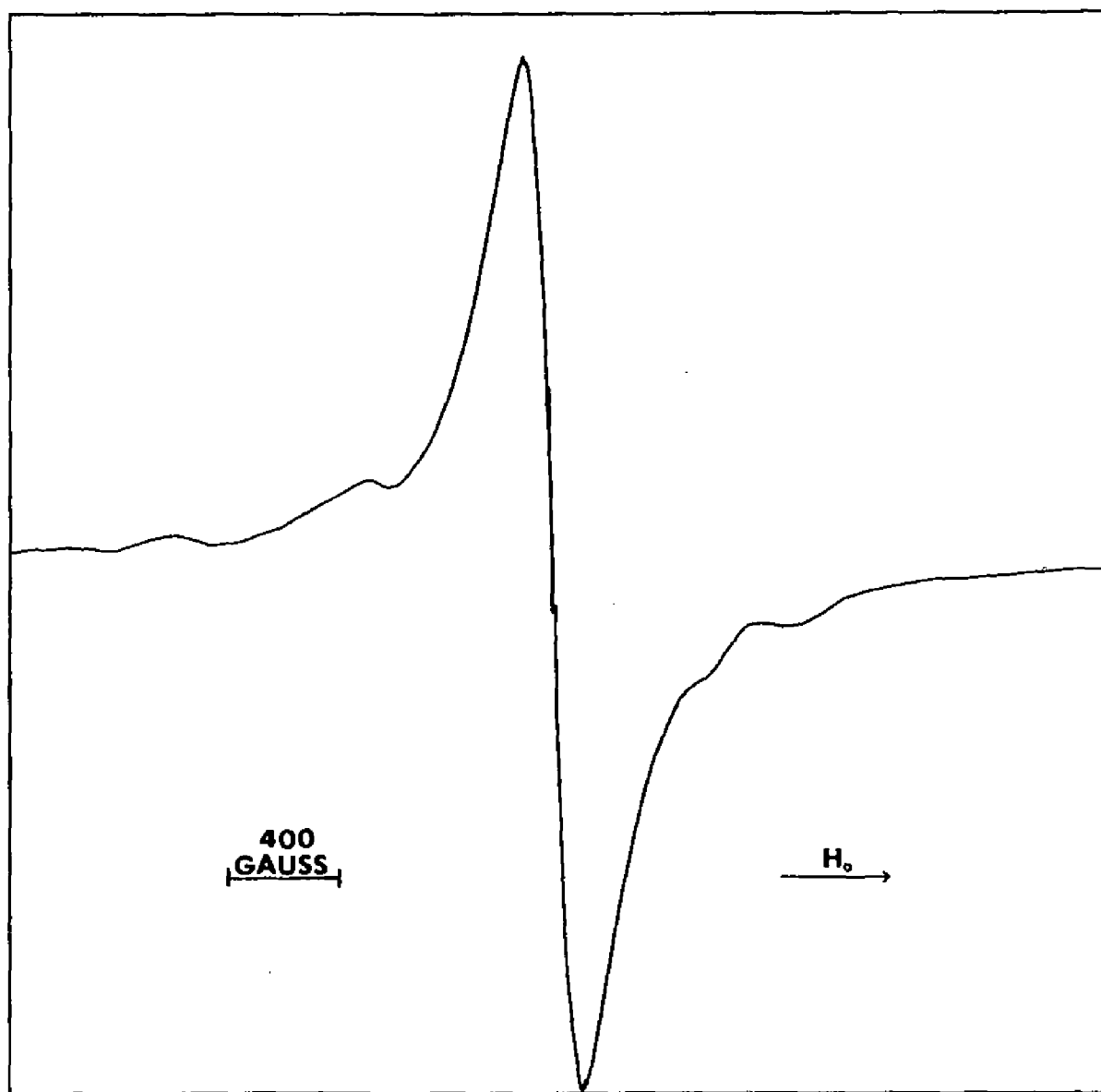


Figure 15. ESR Spectrum of $(\text{Et}_4\text{N})_2\text{CrOF}_5$ in the Solid State.

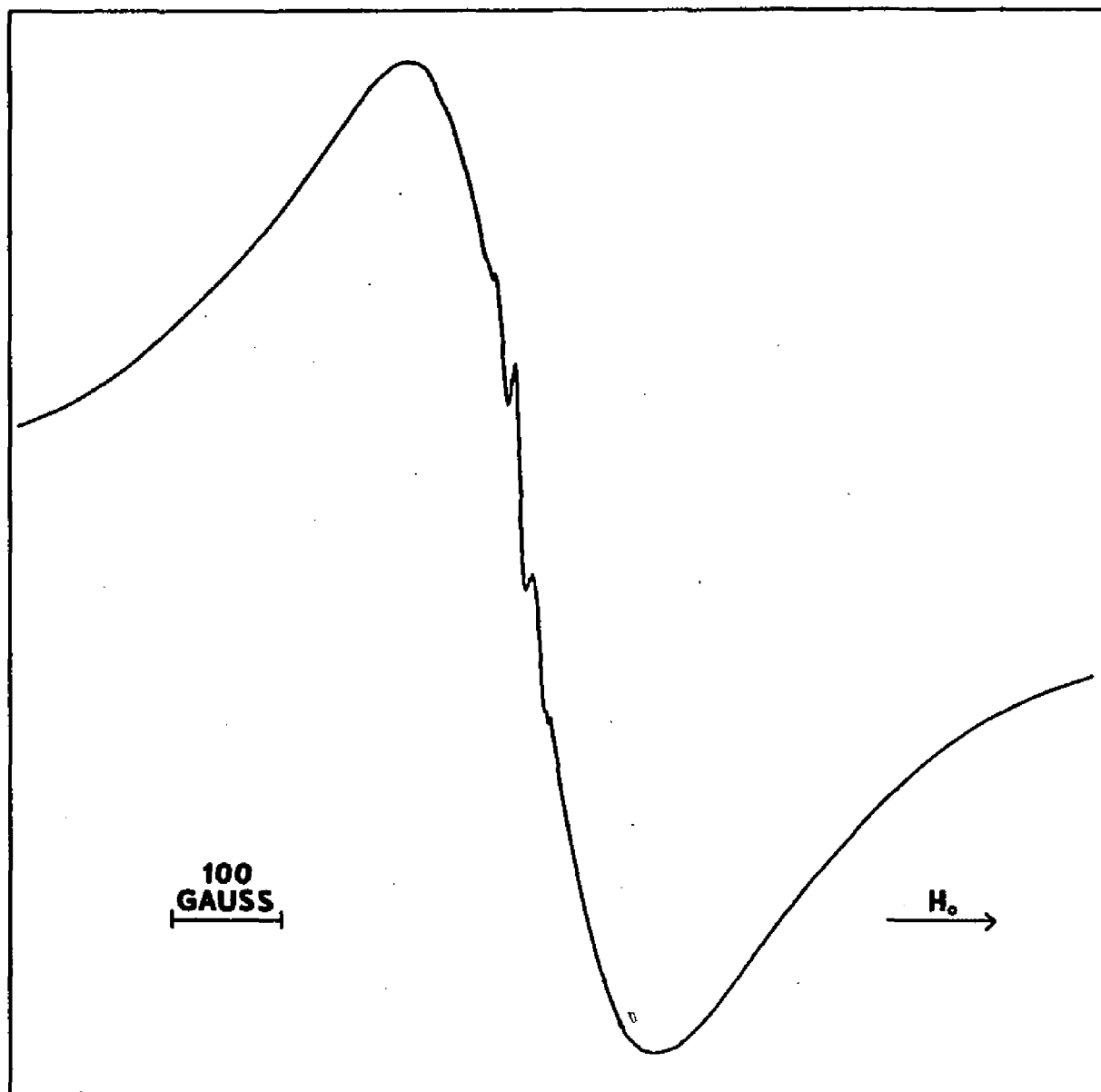


Figure 15a. ESR Spectrum of $(\text{Et}_4\text{N})_2\text{CrOF}_5$ in the Solid State.

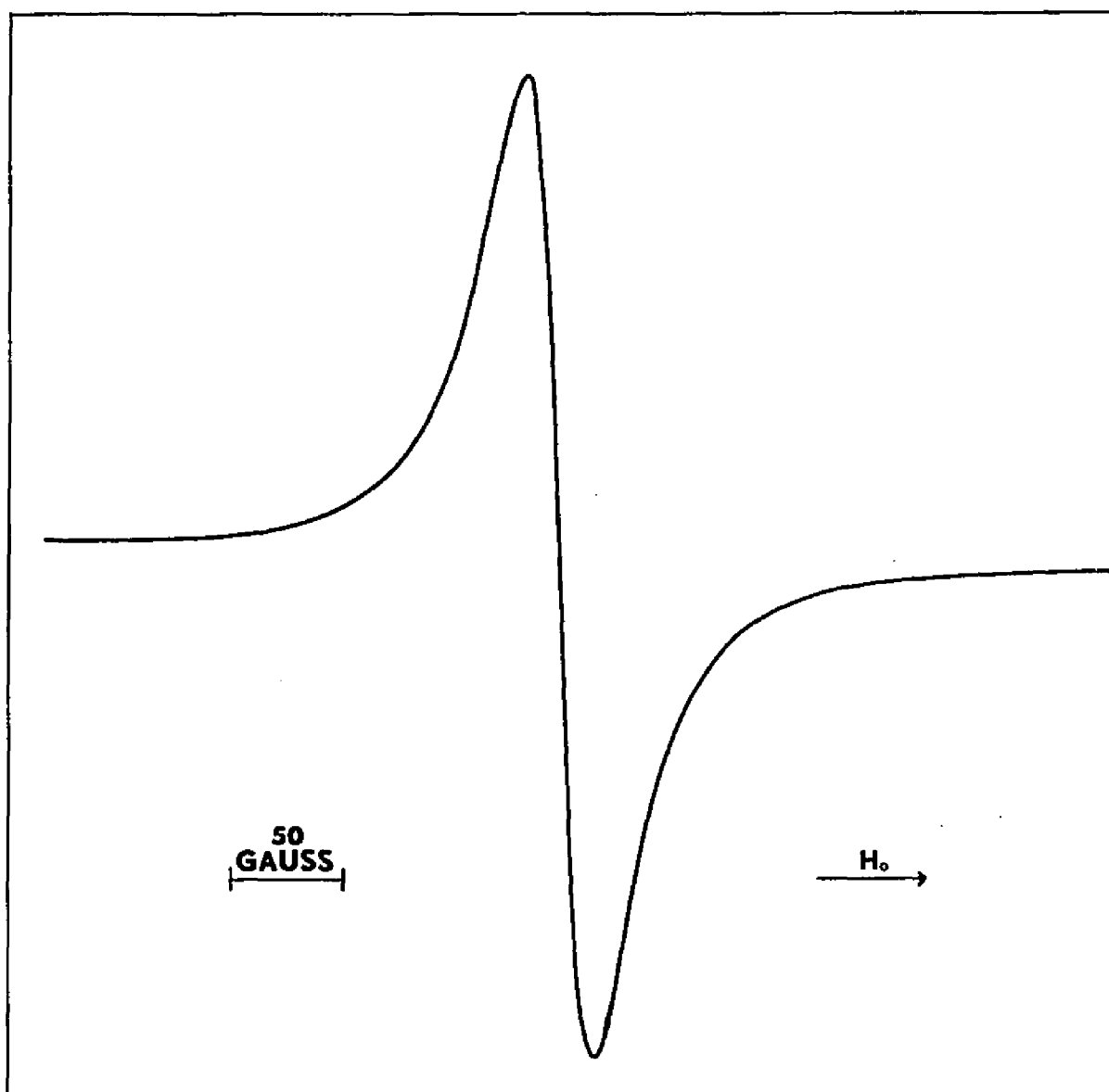


Figure 16. ESR Spectrum of $\text{Cs}_2\text{CrO}(\text{tart})\text{Cl}_3$ in the Solid State.

TABLE VIII
ESR PARAMETERS AND SPIN-ORBIT COUPLING CONSTANTS OF
OXOCHROMIUM(V) AND SOME OXOMOLYBDENUM(V) COMPLEXES

Species	$\langle g \rangle$	$g_{ }$	g_{\perp}	$\xi(\text{cm}^{-1})$	Ref. (a)
CrOF_4^-	1.964	1.959	1.968	---	43
CrOF_5^{2-}	1.963	1.959	1.968	---	43
$(\text{Et}_4\text{N})_2\text{CrOF}_5$	1.968	1.961	1.975	115	
MoOF_5^{2-}	1.905	1.874	1.911	---	43
$(\text{NH}_4)_2\text{MoOCl}_5$	1.947	1.915	1.965	240	28
K_2CrOCl_5	---	2.008 ₅	1.977 ₃		34
$\text{Rb}_2\text{CrOCl}_5$	1.988 1.986	1.980 1.978	1.995 1.990	48 65	28
$\text{Cs}_2\text{CrOCl}_5$	1.988	1.982	1.994	47	
$\text{Me}_4\text{NCrOCl}_4$	1.9875 1.990	---	---	---	34
$\text{Et}_4\text{NCrOCl}_4$	1.987	1.979	1.994	53	
$\text{Pr}_4\text{NCrOCl}_4$	1.987	1.980	1.994	51	
$\text{Bu}_4\text{PCrOCl}_4$	1.984	1.975	1.992	63	
$(\text{C}_6\text{H}_5)_4\text{AsCrOCl}_4$	1.985	1.975	1.993	62	
$(\text{C}_6\text{H}_5\text{CH}_2)(\text{C}_6\text{H}_5)_3\text{PCrOCl}_4$	1.988	1.981	1.995	47	
$\text{Cs}_2\text{CrO}(\text{tart})\text{Cl}_3$	1.969	1.954 1.947	1.980 1.983	124 141	(b)
$\text{Cs}_2\text{CrO}(\text{C}_3\text{H}_2\text{O}_5)\text{Cl}_3$	1.986	1.980 1.978	1.992 1.993	58 64	(b)
$\text{CsCrO}(\text{C}_4\text{H}_4\text{O}_5)\text{Cl}_3$	1.973	1.959 1.955	1.983 1.985	108 119	(b)

(a) Whatever data are not specifically referenced come from this work
(All data obtained from solid state spectra).

(b) The first listed values of $g_{||}$, g_{\perp} and ξ for each of these compounds was calculated using the lower energy band of the split $xy \rightarrow xz, yz$ transition and the second listed values come from using the higher energy band of this pair.

presence of two different types of fluorine atoms, namely the axial and equatorial fluorines. The intensity of the band due to the equatorial fluorines, of course, should be greater than that due to the axial fluorine.

In Table VII, values for $g_{||}$, g_{\perp} and ξ , spin-orbit coupling constant are listed for the oxochromium(V) species and also for some oxomolybdenum(V) complexes. The values obtained from compounds prepared in this study were calculated from simultaneous solutions of the equations given by Ballhausen and Gray²⁶, equations 1, 2 and 3 on page 9 of this dissertation. There are a number of points that are of interest in the parameters obtained in this study in comparison to other published work. (1) It is of interest to note that for all of the compounds prepared in this study $g_{||} < g_{\perp}$ including the fluoro-complex. This is in marked contrast to the work of Kon and Sharpless³⁴ whose studies showed $g_{||} > g_{\perp}$ for the chloro-complexes. (2) The values of $g_{||}$ and g_{\perp} are lower for the fluoro-complex than for the corresponding chloro-complexes and this is also true for the fluoro and chloro-complexes of oxomolybdenum(V)⁴⁸. (3) The spin-orbit coupling constant for the fluoro-complex is higher than those for the chloro-complexes. This is what one would predict because as the covalency of the bonds in a complex increase the spin-orbit coupling constant decreases. (4) In most cases ξ is less in the CrOCl_5^{2-} than in the CrOCl_4^- species. This seems reasonable in light of the fact that there is one more Cr-Cl covalent bond in CrOCl_5^{2-} than in CrOCl_4^- .

DISCUSSION

(A) Infrared Spectra

In the infrared spectra of the new complexes of Cr(V) prepared in this study, there are two regions that are of major importance. The first region is that of the chromium-multiply bonded oxygen stretching frequency and the second involves the region of the chromium-chlorine stretching frequency. As was indicated earlier the region of absorption for the oxocations ordinarily occurs in the range $900-1100\text{ cm}^{-1}$ ⁽⁵⁴⁾ and the intensity of this metal-oxygen band is usually much greater than that of any surrounding bands. This appears to be the case with the M_2CrOCl_5 (M = Rb or Cs) species where the Cr-O band occurs at 945 cm^{-1} for both species. This band remains in approximately the same position whether observed in a Nujol mull sample or in a KBr pellet matrix.

For the new RCrOCl_4 species prepared here, ordinarily two new bands arise in the NaCl region over what is observed for the chloride salt of the organic cation, R^+ . This data is summarized in Table IX. One band occurs in the range $940-965\text{ cm}^{-1}$ while the second occurs in the range $1005-1035\text{ cm}^{-1}$. In KBr or KCl pellets these same species exhibit a very strong band in the $945-960\text{ cm}^{-1}$ region and a very weak band in the $1005-1035\text{ cm}^{-1}$ region.

In order to try to distinguish which of these two bands is the Cr(V)-O stretching frequency, the compounds were allowed to stand in the open air for a number of hours until it appeared that

TABLE IX
STRETCHING FREQUENCIES ASSIGNED FOR THE
OXOCHLOROCHROMIUM(V) COMPOUNDS (cm^{-1})

Compound	Cr(V)-O	Cr(VI)-O	Cr-Cl
$\text{Rb}_2\text{CrOCl}_5$	945(s) ^a		320(s)
$\text{Cs}_2\text{CrOCl}_5$	945(s) ^b		340(s) ^b
$\text{Me}_4\text{NCrOCl}_4$	1020(s)		400(s)
$\text{Et}_4\text{NCrOCl}_4$	1035(s)	960(m)	400(s)
$(\text{Pr})_4\text{NCrOCl}_4$	1005(s)	965(m)	410(s)
$\text{Bu}_4\text{PCrOCl}_4$	1025(s)	950(w)	385(s)
$(\text{C}_6\text{H}_5\text{CH}_2)(\text{C}_6\text{H}_5)_3\text{PCrOCl}_4$	1020(m)	940(s)	415(m)
$(\text{C}_6\text{H}_5)_4\text{AsCrOCl}_4$	1020(m)	940(w)	390(s)

^aBands obtained from Nujol mulls using CsI optics.

^bBrown³⁷ reported 925 for the Cr-O and 336 for the Cr-Cl bands.

all or most of the Cr(V) had been oxidized, and then the infrared spectra were recorded again in Nujol mulls. In all cases the band that had appeared in the $1005\text{-}1020\text{ cm}^{-1}$ region diminished appreciably in intensity, whereas the band in the $940\text{-}965\text{ cm}^{-1}$ region was still present. Therefore it may be presumed that the latter band is possibly due to a Cr(VI)-O stretching mode. The asymmetric Cr(VI)-O stretching mode in the CrO_3Cl^- species has been reported to occur at 950 cm^{-1} ⁴⁶, which supports the hypothesis that the $940\text{-}965\text{ cm}^{-1}$ band observed in the RCrOCl_4 species is actually due to a Cr(VI) species formed by the facile oxidation of the RCrOCl_4 compound. During the preparation of a KCl pellet or a KBr pellet of the RCrOCl_4 species it seems logical to assume that a chloride ion or bromide ion may occupy the open sixth octahedron position in the square pyramidal CrOCl_4^- species. This, of course, would produce the same species contained in the compounds, M_2CrOCl_5 . Therefore, the Cr-O band should shift when the infrared spectrum of a RCrOCl_4 compound is observed in the pellet form. However, when one compares this to results obtained with the corresponding oxotetrachloromolybdate(V), MoOCl_4^- , and the oxopentachloromolybdate(V), MoOCl_5^{2-} , one must conclude that oxidation also is occurring during the preparation of the pellet containing the chromium species. The infrared spectrum of $\text{Et}_4\text{NMoOCl}_4$ was recorded in Nujol mull and in KBr pellet. In both cases an intense sharp band was observed at 1005 cm^{-1} which is the region that the Mo-O band is ordinarily found.

Therefore if occupancy of the open sixth octahedral position occurred one would expect the Mo-O band to shift down to the frequency of approximately 952 cm^{-1} which is the position of the Mo-O band in the compound, $\text{Cs}_2\text{MoOCl}_5$ ⁶⁵. However, since this shift in the Mo-O band does not occur in going from the Nujol mull to the pellet it seems logical to assume that the corresponding MoOCl_5^{2-} species does not form during preparation of a pellet starting with the MoOCl_4^- species.

Piovesana and Furlani⁴⁷ noted a similar difference in the Mo-O stretching frequency when changing from the MoOCl_5^{2-} to the MoOCl_4^- species. The maximum difference was observed between $\text{Cs}_2\text{MoOCl}_5$, where the Mo-O stretching frequency occurs at 955 cm^{-1} , and $\text{Bu}_4\text{NMoOCl}_4$ for which the stretching frequency is $1000\text{-}1015\text{ cm}^{-1}$. The Mo-O stretching frequency was also observed in the compound, $\text{Et}_4\text{NMoOCl}_4$ to be at 1000 cm^{-1} ; so it appears that the coordination number of the metal makes a considerable difference in the position of the M-O (M = Cr or Mo) multiple bond stretching frequency.

One other example of the same effect is noted in that the V-O stretching frequency in VOF_5^{3-} is found at a lower frequency than in VOF_4^{2-} . This is in accordance with the observation^{66,67} that the occupation of the site trans to the vanadyl oxygen reduces

⁶⁵ Sabatini, A., and Bertini, I., Inorg. Chem., 5, 204 (1966).

⁶⁶ Nakamoto, K., Morimoto, Y., and Martell, A.E., J. Am. Chem. Soc., 83, 4533 (1961).

⁶⁷ Sathyanarayana, D.N., and Patel, C.C., Bull. Chem. Soc. Japan, 37, 1736 (1964).

the V-O frequency due to a decrease in the $p_{\pi}-d_{\pi}$ donation from oxygen to vanadium. In other words, a trans ligand weakens the metal-oxygen bond.

The second assignment of the infrared bands recorded for the oxochlorochromate(V) species involves the Cr-Cl stretching mode. Brown³⁷ assigned the band recorded at 336 cm^{-1} for the $\text{Cs}_2\text{CrOCl}_5$ compound to the Cr-Cl stretching vibration but the position of this band in the CrOCl_4^- species has not been published. As one can see in Table IX, there is a large shift in the Cr-Cl stretching frequency as one goes from the CrOCl_5^{2-} species to the CrOCl_4^- species. This sort of shift of the M-Cl stretching frequency is not without precedence. Clark⁶⁸ observed this type of shift in a series of titanium(IV) and vanadium(IV) complexes where the M-Cl stretching frequency changes sharply as the coordination number of the metal changes. This data is summarized in Table X. Such a relationship would be expected, because in general, bond lengths increase (due to overall bond weakening) as the coordination number of the metal increases. The CrOCl_5^{2-} and CrOCl_4^- species fit nicely into this scheme and from the large shift in the Cr-Cl stretching frequency in the two species it would appear that the Cr-Cl bond strength is considerably greater in the CrOCl_4^- species than the CrOCl_5^{2-} species. This may have been a contributing factor in the many unsuccessful attempts here to prepare new Cr(V) complexes from

⁶⁸Clark, R.J.H., Spectrochim. Acta, 21, 955 (1965).

TABLE X

DEPENDENCE OF $\nu(\text{TiCl})$ AND $\nu(\text{VCl})$ VIBRATIONAL FREQUENCIES
ON THE COORDINATION NUMBER OF THE METAL (cm^{-1})

Compound	C.N.	$\nu(\text{MCl})^a$
TiCl_4	4	490
$\text{TiCl}_4 \cdot 2\text{L}$	6	~380
$\text{TiCl}_4 \cdot 2\text{D}$	8	317
VCl_4	4	482
$\text{VCl}_4 \cdot 2\text{L}$	6	~370
$\text{VCl}_4 \cdot 2\text{D}$	8	317

^a TiCl_4 and VCl_4 recorded as liquids; the remaining were recorded as Nujol mulls; L = monodentate ligand; D = o-phenylene bis-dimethylarsine.

the RCrOCl_4 species. No great success was achieved using $\text{Cs}_2\text{CrOCl}_5$ either, but it did form three new complexes with hydroxy acids while this did not occur with RCrOCl_4 . Therefore, this success also leads one to believe that it is easier to replace the chloride ions in the $\text{Cs}_2\text{CrOCl}_5$ compound with some other ligand than in the RCrOCl_4 compounds.

Since RCrOCl_4 and R_2CrOCl_5 are prepared by the same procedure, it is worthwhile to point out what appears to be the largest factor involved in determining which of the two complexes will be obtained in a given preparation. The largest contributing factor appears to be the size of the cation used in the RCl salt which causes precipitation of the CrOCl_4^- or CrOCl_5^{2-} species. Note that with such cations as K^+ , Rb^+ , Cs^+ , and NH_4^+ the R_2CrOCl_5 species is formed but when such cations as R_4N^+ , R_4P^+ , and R_4As^+ are used one invariably gets the RCrOCl_4 species. The largest cation that is known to form the R_2CrOCl_4 species is the Cs^+ ($r = 1.67\text{\AA}$) while the smallest cation that is known to form the RCrOCl_4 species is the Me_4N^+ ($r = 3.4\text{\AA}$).

Piovesana and Furlani⁴⁷ also recently reported that formation of MoOCl_5^{2-} or MoOCl_4^- species depend strongly on the nature of the cation rather than on the preparation method. They noted that with the tetrasubstituted ammonium or arsonium cations the RMoOCl_4 species was obtained even by different preparation procedures.

In summarizing the infrared data of the oxochlorochromate(V) compounds, there is a significant difference in the position of the

Cr-O stretching frequency of the two types of species and likewise in the Cr-Cl stretching frequency which can be attributed, at least partially, to the change in coordination number of the chromium. The particular species that one obtains in preparation depends on the size of the cation where the critical size seems to lie somewhere between the Cs^+ ($r = 1.67\text{\AA}$) and the Me_4N^+ ($r = 3.4\text{\AA}$).

$(\text{Et}_4\text{N})_2\text{CrOF}_5$

No previous infrared data for oxofluorochromium(V) complexes have been reported. Examination of the infrared spectrum of $(\text{Et}_4\text{N})_2\text{CrOF}_5$ shows four bands that are not present in the Et_4NF salt. These bands occur at 960(s), 890(s), 480(m), and 450(m) cm^{-1} .

Sathyanarayana and Patel⁶⁹ assigned the V-F stretching frequency in $(\text{NH}_4)_3\text{VOF}_5$ to the 940 cm^{-1} band and the band at 735 cm^{-1} was assigned the V-F (axial) stretching mode. They also observed a band at 955 cm^{-1} and assigned this to the V-O stretch. However, the assignments of the 940 and 735 cm^{-1} bands were questioned by Piovesana and Selbin⁷⁰ who believed that the two bands in the 900-1000 cm^{-1} region for $(\text{NH}_4)_3\text{VOF}_5$ both arise from the trans F-V=O grouping while bands at 735, 490, and 315 cm^{-1} were believed to be associated with the fundamental molecular vibrations involving primarily V-F bonds

⁶⁹Sathyanarayana, D.N., and Patel, C.C., J. Inorg. and Nucl. Chem., 30, 207 (1968).

⁷⁰Piovesana, O., and Selbin, J., J. Inorg. Nucl. Chem., 31, 433 (1969).

and their stretching and bending motions. Therefore it seems reasonable to assign the two bands observed at 960 cm^{-1} and 890 cm^{-1} in $(\text{Et}_4\text{N})_2\text{CrOF}_5$ to the F-Cr=O asymmetric stretching mode and F-Cr=O symmetric stretching mode, respectively. The bands at 480 cm^{-1} and 450 cm^{-1} may be associated with the Cr-F stretching and bending modes.

An alternate approach is to assign the band at 960 cm^{-1} to the Cr-O stretching mode since this is the most intense band in the spectrum and it occurs in the region where a Cr-O band is ordinarily found. However, in this approach the assignment of the Cr-F band is not quite so obvious. It could be rationalized that the strong band which occurs at 890 cm^{-1} is a Cr-F stretching mode. Hobbs⁷¹ assigned the band at 789 cm^{-1} as the Cr-F stretching frequency in the compound, CrO_2F_2 , and it seems possible that with one less oxygen in the molecule the Cr-F stretching frequency could go as high as 890 cm^{-1} . The Mo-F stretching frequency reported for MoF_6 occurs at 741 cm^{-1} while that for WF_6 occurs at 712 cm^{-1} . Therefore due to the difference in mass of the chromium atom and molybdenum atom one would predict that the Cr-F stretching frequency should be higher than the Mo-F stretching frequency. When a large difference in mass occurs this generally will increase the position of the M-F stretching frequency. For example, the S-F stretching frequency in SF_6 is at 940 cm^{-1} while that for SeF_6 occurs at 780 cm^{-1} .⁷² The

⁷¹Hobbs, W.E., J. Am. Chem. Soc., 28, 1220 (1958).

⁷²Nakamoto, K., "Infrared Spectra of Inorganic Coordination Compounds", John Wiley and Sons, New York, N.Y., 1963.

selenium atom is about $2\frac{1}{2}$ times heavier than the sulfur atom while the Mo atom is not quite twice as heavy as the Cr atom. Therefore, if the same type of increase occurs in going from Mo to Cr that occurs when going from Se to S the Cr-F band could reasonably be the one that occurs at 890 cm^{-1} .

However, the author believes that the first approach seems to be more reasonable since the vibrations along the z axis have got to involve both the oxygen and the axial fluoride. This should give rise to a pseudo-symmetric and a pseudo-antisymmetric stretching vibration along the Cr-O axis.

(B) Visible-UV Spectra

In a d^1 system such as oxochromate(V) four d-d transitions are possible with two of these usually being degenerate particularly in C_{4v} symmetry. The following transitions are possible: $(d_{yz}, d_{xz}) \leftarrow d_{xy}$ (these may be split into two bands by lower symmetry), $d_{x^2-y^2} \leftarrow d_{xy}$ and $d_{z^2} \leftarrow d_{xy}$. The intensities of the ligand field transitions are generally quite low with the extinction coefficients always less than 500, and usually the values are of one order of magnitude smaller than this.

The first and probably the most definite assignment which can be made is $(d_{yz}, d_{xz}) \leftarrow d_{xy}$ to the broad weak band centered at about 12.5kK in acetonitrile in each of the oxochlorochromate(V) species. The molar extinction coefficient for this band is

approximately 20 and it is the lowest energy band observed. This assignment is consistent with that of Gray and Hare²⁷ who assigned the band observed at 12.9kK in the compound, $(\text{NH}_4)_2\text{CrOCl}_5$, to this transition. It is interesting to note at this point that the first band observed in each of the oxochlorochromate(V) complexes ($\text{Cs}_2\text{CrOCl}_5$ and RCrOCl_4 species) occurs at just about the same position in solution. This could indicate two things. First, the chloride in the axial position in $\text{Cs}_2\text{CrOCl}_5$ compound could be ionizing in solution so that the solid tetrachloro and pentachloro species become approximately the same in solution; and the second possibility is that the axial chloride has essentially no effect on the $(d_{yz}, d_{xz}) \leftarrow d_{xy}$ transition because of the strong Cr-O bond. The conductivity data suggests that the $\text{Cs}_2\text{CrOCl}_5$ compound dissociates in more than a 2:1 ratio in acetonitrile, as was mentioned previously, with the axial chloride dissociating and forming CrOCl_4^- . The spectrum of $\text{Cs}_2\text{CrOCl}_5$ was observed after a large excess of Et_4NCl had been added to the solution. The position of the first band did not change nor did the intensity change significantly. With a chloride ion occupying the axial position the species should be much closer to a regular octahedron and hence the d-d transition should be more forbidden by symmetry arguments. Therefore one would expect a lower intensity of these bands for CrOCl_5^{2-} than for CrOCl_4^- . While this expected change in intensity does not occur when Et_4NCl is added to a solution of $\text{Cs}_2\text{CrOCl}_5$, there is a significant change in intensity

of this first band when Et_4NCl is added to a solution of $\text{Et}_4\text{NCrOCl}_4$. The extinction coefficient decreases by approximately a factor of two when there is a 5/1 mole ratio of $\text{Et}_4\text{NCl}/\text{Et}_4\text{NCrOCl}_4$ but the position of the band does not change. A similar change in the intensity was not observed when Et_4NClO_4 was added to a solution of $\text{Et}_4\text{NCrOCl}_4$. Therefore from the above observations it does not appear that the occupation of the axial position can be increased by addition of Et_4NCl to a solution of $\text{Cs}_2\text{CrOCl}_5$ but this will occur to some extent in a solution of $\text{Et}_4\text{NCrOCl}_4$. The solution spectra seem to be indicative of the fact that when the axial position is occupied a red shift is observed in the first band. For example, in a Nujol mull at room temperature the first band in the spectrum of $(\text{C}_6\text{H}_5)_4\text{AsCrOCl}_4$ occurs at 13.54kK, whereas in a good coordinating solvent such as acetonitrile this first band occurs at 12.44kK. One other point of significance which adds to the conclusion that occupation of the axial position does indeed cause the first band to shift to lower energy is the fact that when the spectra of the RCrOCl_4 species are observed in methylene chloride and acetonitrile the first band shifts to a lower energy in acetonitrile when compared to methylene chloride. Of course, acetonitrile is a much better coordinating solvent than methylene chloride so this shift in the first band should be expected.

In the low temperature spectra of the oxochlorochromate(V) complexes the first band is found to be split into three or more components. This splitting could result from two origins: (1) an

electronic origin in that the d_{xz} and d_{yz} orbitals are degenerate only in a rigorously C_{4v} environment and they should be split into two electronic levels in any lower symmetry; and (2) a vibrational origin in that the ungerade vibrational modes of the complex ion and particularly the Cr-O vibration (along the z axis and hence affecting the d_{xz} and d_{yz} orbitals) may also result in a band splitting. The magnitude of the splitting arising from the V-O stretching mode was estimated by Piovesana and Selbin⁷⁰ to be at $600-800\text{ cm}^{-1}$, on the basis that the V-O stretching mode in the ground state of the molecule is in the $900-1000\text{ cm}^{-1}$ region. Therefore the magnitude of the splitting arising from the Cr-O stretching mode should be very similar. It seems likely that the splitting actually observed in the first band must be vibrational in origin. The splitting observed in most cases falls in the range from $600-800\text{ cm}^{-1}$, and likewise in the two cases where the symmetry is most surely C_{4v} ($\text{Rb}_2\text{CrOCl}_5$ and $\text{Cs}_2\text{CrOCl}_5$) mechanism (1) should not be operative and the splitting should not be observed if they were purely electronic in nature. Similar splittings were observed in $\text{Et}_4\text{NMoOCl}_4$ as well as for other MoO^{3+} species and these were also assigned to a vibrational origin.

One other point worthy of discussion at this time is the position of the first band in the various oxochlorochromate(V) complexes when observed at low temperature in a Nujol mull. In referring back to Figure 4 and 5, a blue shift of about 2.6kK is

observed in the first band when going from $\text{Cs}_2\text{CrOCl}_5$ to $(\text{C}_6\text{H}_5)_4\text{AsCrOCl}_4$. It should also be observed from Table V that a smaller shift of the first band occurs within the RCrOCl_4 species and also within the R_2CrOCl_5 species. Therefore, it seems that the particular cation involved in each species has a small affect on the position of the first band. This presumably must be a secondary coordination sphere affect. Unfortunately, it has not been possible up to the present time to produce a CrOCl_4^- and a CrOCl_5^{2-} species with the same cation.

A shift of 2.6kK for the first band in going from $\text{Cs}_2\text{CrOCl}_5$ to $(\text{C}_6\text{H}_5)_4\text{AsCrOCl}_4$ seems much too large to be caused by such a secondary affect alone. The $(d_{yz}, d_{xz}) \leftarrow d_{xy}$ transition should be quite sensitive to changes in the bond order of Cr-O, or more generally to tetragonality effects. The bond order of the Cr-O bond should be lower in the $\text{Cs}_2\text{CrOCl}_5$ than in $(\text{C}_6\text{H}_5)_4\text{AsCrOCl}_4$ species due to the presence of an axial chloride in the $\text{Cs}_2\text{CrOCl}_5$ species. Therefore it seems logical that the tetragonality effect is somewhat greater in the CrOCl_4^- than the CrOCl_5^{2-} species which should cause a greater energy gap between the d_{xy} and the $d_{xz, yz}$ orbitals. Hence it seems reasonable to expect the first band in the $\text{Cs}_2\text{CrOCl}_5$ compound to appear at a slightly lower energy than the first band in $(\text{C}_6\text{H}_5)_4\text{AsCrOCl}_4$.

A sixth ligand would be expected to decrease the energy of the $(d_{yz}, d_{xz}) \leftarrow d_{xy}$ transition. The weakening of the Cr-O σ -bond would cause the oxygen to move out from the chromium and also weaken the π -bonds, which primarily involve the d_{xz} and d_{yz} orbitals. Likewise, a decrease in the $\text{O-Cr-Cl}_{\text{eq}}$ bond angle would also decrease

any π -bonding between the equatorial ligands and the d_{xz}, d_{yz} orbitals. A still stronger ligating agent such as F^- would be expected to cause both of these effects in larger degree and thus shift the $(d_{yz}, d_{xz}) \leftarrow d_{xy}$ transition to still lower energies.

The spectral data from the solid state further supports the data from the solution spectra and more firmly establishes the observation that the occupation of the axial position does indeed cause a red shift in the first band as the foregoing discussion shows one would expect.

In the visible-ultraviolet spectrum of $(Et_4N)_2CrOF_5$ in Nujol mull at $77^\circ K$ the first broad low intensity band is centered at approximately $8.35kK$. To be consistent with the data and band assignments for the oxochlorochromate(V) species and likewise with the chloro and fluoro species of both VO^{2+} and MoO^{3+} , the assignment of this band must be to the $(d_{yz}, d_{xz}) \leftarrow d_{xy}$ transition. To repeat, it was to be expected that the $(d_{yz}, d_{xz}) \leftarrow d_{xy}$ transition should occur at a lower energy for the fluoro complex than for the chloro complex.

One other point of interest with this first band is the fact that it appears to be split into two components at $77^\circ K$. The two peaks that are observed in the first band are split by only 120 cm^{-1} whereas in the chloro complexes the first band in the spectra is split into several peaks separated anywhere from $600\text{--}800\text{ cm}^{-1}$. Therefore, it does not seem likely that the splitting in the first band of the fluoro complex is vibrational in nature, as it appears to

be in the chloro complexes. Likewise because of the high symmetry it appears very unlikely that these two components are caused by the splitting of the d_{xz} and d_{yz} orbitals.

The second band that occurs in the oxochlorochromate(V) species is observed at approximately 18kK both in solution and in the solid state. The molar extinction coefficient for each of the compounds (RCrOCl_4 and R_2CrOCl_5) is something less than 100 in acetonitrile. As is evident from Table V the position of this band is relatively constant regardless of the cation present and it should also be noted that this band is never found to be split. Therefore, it seems quite probable that this second band is the $d_{x^2-y^2} \leftarrow d_{xy}$ transition, making it then a measure of $10Dq$. In an electronic transition, primarily between a non-bonding non-degenerate orbital (d_{xy}) and an antibonding non-degenerate orbital ($d_{x^2-y^2}$) neither of which is involved with the strongly bound oxo-oxygen one would not expect a splitting to occur, unless it were to arise from the coupling of the electronic transition with a Cr-Cl vibrational mode.

It is interesting to note that there is no significant difference in the position of this band whether the species is CrOCl_4^- or CrOCl_5^{2-} . There are a number of distinct effects that should occur whenever a sixth ligand attaches trans to the oxo-oxygen. Of course, these effects are not separately observable since they occur simultaneously and in opposing ways. The effects include (1) lowering of the individual bond energies of all of the other bonds by ligand

and electron pair repulsions; (2) weakening of the oxo-oxygen bond by utilizing a "portion" of the same orbitals (d_{z^2} , p_z , d_{xz} , d_{yz}) presumed to bond only the oxo-oxygen in the pentacoordinated species; (3) strengthening of equatorial σ -bonding to the $d_{x^2-y^2}$ orbital inasmuch as greater ligand σ -orbital overlap is possible with this orbital when the equatorial ligands are forced by the sixth ligand to move up closer to the plane normal to the Cr-O bond and containing the Cr atom; (4) weakening of any π -bonding involving the equatorial ligand π -orbitals and the $\pi(d_{xz}, d_{yz})$ chromium orbitals; and (5) strengthening of any π -bonding involving equatorial ligands and the d_{xy} orbital.

If the band which occurs at 18kK corresponds to the $d_{x^2-y^2} \leftarrow d_{xy}$ transition, the 10Dq value should be expected to have a value appropriate to fit with those of the corresponding VO^{2+} and MoO^{3+} complexes. Generally, the 10Dq value for a plus three ion is 40-80% larger than that for a plus two ion. Hence, the 10Dq value for CrO^{3+} should be that much larger than the 10Dq value of the corresponding VO^{2+} species. Likewise from a 3d to a 4d transition metal the 10Dq value for a 4d transition metal is generally 30-50% larger than that for a corresponding 3d transition metal. Therefore, we should expect to find this increase in the 10Dq value on changing from CrO^{3+} to MoO^{3+} . The results of this comparison are given in Table XI. It can be seen that the increase in 10Dq from VO^{2+} to CrO^{3+} is approximately 53%; and the increase in the 10Dq value from CrO^{3+} to MoO^{3+} is not quite as large as expected but it is certainly

not very much less than 30%.

TABLE XI

COMPARISON OF $d_{x^2-y^2} \leftarrow d_{xy}$ TRANSITION OF THE CHLORO-COMPLEXES
OF VO^{2+} , CrO^{3+} AND MoO^{3+}

Species	$d_{x^2-y^2} \leftarrow d_{xy}$	% Increase	Reference
VO^{2+}	11,750 cm^{-1}		70
CrO^{3+}	18,000 cm^{-1}	53%	this work
MoO^{3+}	23,000 cm^{-1}	28%	27

This second band, at 18kK, was not observed by Gray and Hare²⁷ in the compound, $(NH_4)_2CrOCl_5$. It is curious and not at all understood why they did not observe this band in the spectrum of the solid.

In the $(Et_4N)_2CrOF_5$ spectrum in Nujol the second band is observed at 14.87kK. If the first two assignments of the bands observed in the oxochlorochromate(V) species are correct the band observed at 14.87kK for the fluoro complex cannot reasonably be assigned to the $d_{x^2-y^2} \leftarrow d_{xy}$ transition. It does not follow that the $10Dq$ value for a fluoro complex should be less than in a corresponding chloro complex. Hence, it seems reasonable to look to the next low intensity band in the spectrum of the fluoro complex

for the $d_{x^2-y^2} \leftarrow d_{xy}$ transition. This band occurs at 22.33kK and the assignment of this band as the $d_{x^2-y^2} \leftarrow d_{xy}$ transition seems reasonable from the standpoint of the 10Dq value for the chloro-complex. This would make the 10Dq value about 4kK larger for the fluoro-complex and this does not seem out of line. The difference observed for the corresponding chloro and fluoro complexes of VO^{2+} is 3.4kK⁷⁰.

For comparison purposes it is interesting to note the positions of the $d_{x^2-y^2} \leftarrow d_{xy}$ transition for the fluoro-complexes of VO^{2+} and the MoO^{3+} . This data is tabulated in Table XII. It

TABLE XII
COMPARISON OF $d_{x^2-y^2} \leftarrow d_{xy}$ TRANSITION OF THE FLUORO-COMPLEXES
OF VO^{2+} , CrO^{3+} AND MoO^{3+}

Species	$d_{x^2-y^2} \leftarrow d_{xy}$	% Increase	Reference
VO^{2+}	15,400 cm^{-1}		70
CrO^{3+}	22,330 cm^{-1}	45%	this work
MoO^{3+}	29,000 cm^{-1*}	30%*	----

* Predicted here.

can be seen that from VO^{2+} to CrO^{3+} the increase in 10Dq is approximately 45%. Unfortunately the band assignments for $MoOF_5^{2-}$ have not been reported in the literature. The only spectral measurements that have been done on what was believed to be the anion, $MoOF_5^{2-}$ present in

diluent crystals, were reported by Wentworth and Piper⁷³. They reported bands at 12.3, 13.1, 21.2 and 22.0kK. Assuming that the 10Dq value for MoOF_5^{2-} is 30% greater than for CrOF_5^{2-} due to the fact that one is going from a 3d to 4d transition metal the $d_{x^2-y^2} \leftarrow d_{xy}$ transition for MoOF_5^{2-} should occur at approximately 29kK.

The third band that is observed in each of the oxochloro complexes of chromium(V) occurs at approximately 22.5kK. In three of the compounds this band is not observed in acetonitrile and in three others it is observed only as a shoulder (see Table V). A possible explanation for this is that the strong band which occurs at approximately 27kK is so intense that it covers the band at 22.5kK. The molar extinction coefficient for this band appears to be in the region of 400-500 but it may be much less than this because of the overlap of the intense band at approximately 27kK. This band is much more clearly defined in Nujol and is observed in all chloro compounds except for the $\text{Cs}_2\text{CrOCl}_5$ complex. For some unknown reason the spectrum of $\text{Cs}_2\text{CrOCl}_5$ reaches a maximum at 18kK and then flattens out in a plateau until the slit opens completely (see Figure 5).

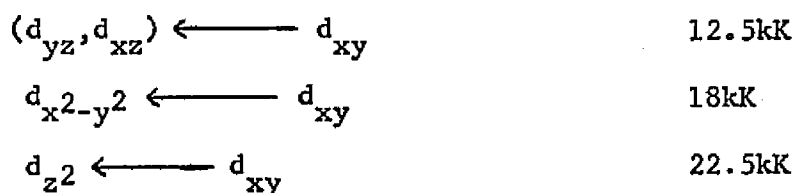
There appear to be at least two possibilities for the assignment of this band. From the rather low intensity and from the position of the band one possibility that must certainly be considered is that it is the $d_{z^2} \leftarrow d_{xy}$ transition. This band, which was found at 23.5kK in $(\text{NH}_4)_2\text{CrOCl}_5$ was assigned to the $d_{x^2-y^2} \leftarrow d_{xy}$ transition

⁷³Wentworth, R.A.D., and Piper, T.S., J. Chem. Phys., 41, 3884 (1964).

by Gray and Hare²⁷; but as was indicated earlier they did not observe the band at 18kK which is assigned here to the $d_{x^2-y^2} \leftarrow d_{xy}$ transition. Kon and Sharpless³⁴, who observed the band at 18kK, did not question the assignment by Gray and Hare²⁷ of the 23.5kK band. However, to explain their ESR determined g values satisfactorily they assigned the band at 18kK to a charge transfer band in which an electron in a filled σ -orbital is excited to the half-filled d_{xy} orbital.

A second possibility for the assignment of the band at 22.5kK in the chloro species is a charge transfer transition from the ligand to the metal, i.e., chloride-to-chromium. This transition arises when one of the electrons in a filled molecular orbital (primarily a ligand pi orbital) is excited to one of the orbitals consisting primarily of a metal d orbital. The possibility also exists that the origin might be a metal-to-ligand transition, but with a plus five charge on the chromium atom already this appears unlikely.

For the moment let us assume that the band at 22.5kK is the $d_{z^2} \leftarrow d_{xy}$ transition and assume then the following three band assignments:



The first mentioned hypothesis can then be checked under the assumption that the simple crystal field model holds by determining values for

Dq, Ds, and Dt from the equations of Ballhausen and Gray²⁶. The energies of these transitions are given in terms of the constants Dq, Ds and Dt in the following way:

$$\begin{array}{ll}
 (d_{yx}, d_{xz}) \longleftarrow d_{xy} & -3Ds + 5Dt \\
 d_{x^2-y^2} \longleftarrow d_{xy} & 10Dq \\
 d_{z^2} \longleftarrow d_{xy} & 10Dq - 4Ds - 5Dt
 \end{array}$$

The terms, Dq, Ds and Dt, are formulated using a crystal field approach⁷³ so that

$$\begin{aligned}
 Dq &= 1/6 \rho_4^{xy} \\
 Ds &= 1/7 (2\rho_2^{xy} - \rho_2^{z+} - \rho_2^{z-}) \\
 Dt &= 1/21 (2\rho_4^{xy} - \rho_4^{z+} - \rho_4^{z-})
 \end{aligned}$$

where $\rho_n = eq \left\langle \frac{r^n}{R^{n+1}} \right\rangle$. Here, e represents the electronic charge and q the effective ligand charge, while R and r are used to delineate the metal ion to ligand and the electron to metal distances, respectively. To insure that these equations are consistent with earlier formulations of Ds and Dt it need only be noted that if both axial ligands exert identical fields the equations reduce to the form predicted by Piper and Carlin⁷⁴ for the centric tetragonal field. If all of the ligands exert the same field Ds and Dt become zero and the equation for Dq is that of a regular octahedral case.

⁷⁴Piper, T.S., and Carlin, R.L., J. Chem. Phys., 33, 1208 (1960).

One significant prediction is stressed by Wentworth and Piper⁷³: D_s and D_t should both be negative quantities. Such a proposal follows from the assumption of the great importance of the field of the lone oxygen. Under these circumstances ρ_n^{z+} must be larger than the other terms. The relative order of magnitude is given in their paper (which dealt with VOCl_5^{3-}) as follows: $\rho_n^{z+} \gg \rho_n^{z-} \sim \rho_n^{xy}$. Hence, it follows that D_s and D_t should be negative.

Simple algebraic solution of the above equations yield $D_q = 1.8\text{kK}$, $D_s = -2.4\text{kK}$ and $D_t = 1.1\text{kK}$. Since D_t is a positive term this seems to eliminate the possibility of assigning the band at 22.5kK to the $d_{z^2} \leftarrow d_{xy}$ transition assuming that the first two assignments are correct.

At this point it will be assumed that the band at 22.5kK is a charge transfer transition. Two proposals have been made concerning the filled molecular orbital having the highest energy in oxochromium(V) species: Gray and Hare²⁷ suggested a π level associated with the oxo group was highest in energy while Kon and Sharpless³⁴ proposed a sigma level associated with bonding of the planar ligands. A third possibility, which was proposed by Allen et al.⁷⁵ for MoO^{3+} species, includes a π chloro level as the highest filled molecular orbital.

Allen et al.⁷⁵ offered considerable evidence for their disagreement with the Gray-Hare scheme. These workers prepared and

⁷⁵Allen, E.S., Birsdon, B.J., Edwards, D.A., Fowles, G.W.A., and Williams, R.G., J. Chem. Soc., 4649 (1963).

performed spectral measurements on a number of oxochloromolybdates(V), oxobromomolybdates(V), and oxochlorotungstates(V). Some of these results are shown in Table XIII.

TABLE XIII
VISIBLE-UV SPECTRAL DATA FOR SOME OXOHALIDE COMPLEXES
OF Mo(V) and W(V) (REFERENCE 75)

Complex	Phase	Peak Position(kK) (Molar extinction coefficient in parentheses)
$M_2^I MoOCl_5$	aq • HCl	14.10(11); 22.42(10); 28.01(570); 32.26(5300); 40.00(3600)
$M_2^I MoOBr$	aq • HBr	14.29(7); 21.28(560); 24.10(3200); 26.53(25.00)
$M_2^I WOCl_5$	aq • HCl	14.20(29); 25.19(16); 32.79(500); 37.17(2700); 44.44(3000)

As one can observe from Table XIII both the $MoOCl_5^{2-}$ and $WOCl_5^{2-}$ species have very similar spectra in that there are two low intensity bands followed by three bands at higher energy which are much more intense. Allen et al.⁷⁵ assigned the first two bands to ligand field transitions, similar to the Gray and Hare²⁷ assignments, and the three bands at higher energy as charge transfer in origin. Note that the first band in both the molybdenum and tungsten complexes occurs in almost the exact same position. Therefore, using the Gray-Hare scheme, it follows that the $b_2 \rightarrow e_{\pi}^*$ energy gap is the same in both complexes. If this were true

one might expect little difference in the energy level of the e_{π}^b orbital in both complexes. Therefore the first two charge transfer bands might be expected to occur at about the same frequency for MoOCl_5^{2-} and WOCl_5^{2-} . However, as one can note from Table XIII all three charge transfer bands for the tungsten complex blue shift by $4000\text{-}5000\text{ cm}^{-1}$. The increase in the second band would be expected because of the increase in $10Dq$ when moving down a family in the transition metals but the large energy shift in the first two charge transfer bands is inexplicable in terms of the Gray-Hare scheme. If the same reasoning is applied in comparing the position of the bands in MoOCl_5^{2-} to those of MoOBr_5^{2-} it is again evident that the data is irreconcilable with the Gray-Hare proposal.

Also, Horner and Tyree⁷⁶ have noted a great similarity in the charge transfer bands of MX_6^- and MOX_5^{2-} (where $M = \text{Nb, Mo, or W}$ and $X = \text{Cl or Br}$). They suggested that this similarity was difficult to explain unless the transition involved molecular orbitals with considerable halogen character.

The second proposal presented by Kon and Sharpless^{34,77} placed a σ -level orbital as the highest energy filled bonding molecular orbital for the CrOCl_5^{2-} species as well as for MoOCl_5^{2-} species. They point out that the metal-oxygen bond is very important and that the strength of the metal-halogen bond is correspondingly weak so that

⁷⁶Horner, S.M., and Tyree, S.Y., Jr., Inorg. Nucl. Chem. Letters, 1, 43 (1965).

⁷⁷Kon, H., and Sharpless, N.E., J. Chem. Phys., 70, 105 (1966).

exciting an electron from a σ -bonding halogen orbital will require less energy than the transition from the pi levels. This suggestion is consistent with the observations of Allen, et al.⁷⁵ but it does not explain the similarity in the charge transfer spectra of MX_6^- and MOX_5^{2-} . If Kon and Sharpless are correct, the absence of the oxo group should drop the σ -bonding level to lower energy and cause a significant change in the spectra.

If the pi orbitals from the chlpro group are highest in energy all of the problems indicated above seem to be avoided. Therefore, it appears that the most reasonable conclusion on the basis of available evidence is that the third band at 22.5kK is a charge transfer transition in which an electron is excited from a chlorine pi-orbital to the d_{xy} orbital of the chromium atom.

It seems reasonable at this point to assign the band at 15kK in the spectrum of $(\text{Et}_4\text{N})_2\text{CrOF}_5$ to the same type of transition, but here from a fluorine pi-orbital to the d_{xy} orbital of the chromium atom. Initially, it appears that the electronegativity order, which is $\text{F}^- > \text{Cl}^-$, should be followed in assigning the charge transfer bands, but the second thought is that this is misleading when applied to optical charge transfer. Since it would most likely be the highest filled pi-orbital of the ligand from which electron transfer from ligand to metal in the lowest energy charge transfer transition would occur, it would seem pertinent to know the respective energies of these pi-orbitals for the fluoride and chloride ions. The valence shell ionization energies (VSIE's) from the 2p and 3p orbitals

of fluoride and chloride ions have been calculated^{78,79}. These values, in kK units, are:

$$\begin{array}{ccc} \text{F}^- & < & \text{Cl}^- \\ 21.9 & & 24.3 \end{array}$$

From the order of the VSIE's it is reasonable that the first charge transfer band in the fluoro complex should occur at a lower energy than in the chloro complex. Piovesana and Selbin⁷⁰ assigned the first charge transfer band in a series of vanadyl complexes of general formula VOX_5^{n+} and noted that the order of this series corresponded to the order of the VSIE's of F^- , Cl^- , and H_2O which were the only ligands of the series where the VSIE's were known. Therefore the assignments made here for the Cr(V) complexes lend additional support for their assignments of the vanadyl complexes.

The next band in the visible-uv spectra of the oxochloro-chromate(V) complexes occurs from 25-30kK and is split very sharply into a series of bands usually separated from one another on the order of $600\text{-}900\text{ cm}^{-1}$. A corresponding transition is observed in the spectrum of the fluoro-complex from 27.30-31.50kK and is split in a similar manner to the band in the chloro complexes. This splitting is observed only in solution for the chloro complexes but occurs both in the solid state and in solution for the fluoro complex. The molar extinction coefficients for the chloro-complexes are 1500 or less in acetonitrile except for $\text{Cs}_2\text{CrOCl}_5$ where the value is 7550 while the

⁷⁸Cusachs, L.C., and Reynolds, J.W., J. Chem. Phys., 43, S160 (1965).

⁷⁹Basch, H., Viste, A., and Gray, H.B., Theoret. chim. Acta (Berl.), 3, 458 (1965).

value for the fluoro-complex is 86 in acetonitrile.

One possibility for the assignment of this band must be the $d_{z^2} \leftarrow d_{xy}$ transition. The molar extinction coefficient seems relatively large for a d-d transition but in this case some increase in intensity would be expected because of the vibrational splitting.

The effect of a sixth ligand on this transition is difficult to analyze. On the one hand a sixth ligand should cause a weakening of the Cr-O σ -bond which would tend to lower the energy of this transition since the d_{z^2} orbital is primarily involved in the Cr-O σ -bond. However, a weak σ -bond is expected to form with the sixth ligand and this would tend to raise the energy of the $d_{z^2} \leftarrow d_{xy}$ transition. Unfortunately, the effect of the sixth ligand on this transition cannot be observed in the chloro-complex because this band is not observed in the solid state and as was mentioned previously the CrOCl_4^- and CrOCl_5^{2-} species are apparently very similar in solution because of the ready ionization of a chloride in the CrOCl_5^{2-} species. However, in the fluoro complex this band is observed in both the solid and solution. As one can see from Table V the position of this band is essentially the same so that it appears that the two opposing affects essentially cancel each other. This is assuming that the CrOF_5^{2-} species ionizes similar to the CrOCl_5^{2-} species. In comparing the chloro species to the corresponding fluoro-complex, this band is blue-shifted slightly in the fluoro compound. This is to be expected because of the stronger σ -bond that would form between the fluoride and the chromium as compared to the Cr-Cl σ -bond.

The splitting of this band must be due to a vibrational

progression. This, again, could be due to the Cr-O stretching frequency which in the ground state is around 950 cm^{-1} , but which is undoubtedly lowered by a few hundred cm^{-1} in the electronic excited state of the molecule. This vibrational progression due to the Cr-O stretching mode would not be unexpected in the $d_{z^2} \leftarrow d_{xy}$ transition since the oxygen lies along the z axis.

In using the equations of Ballhausen and Gray²⁶ the values calculated for the chloro-complex for Ds and Dt are -2.8kK and +0.82kK while those for the fluoro complex are -2.1kK and +0.32kK, respectively. As was indicated earlier these values, as was emphasized by Wentworth and Piper⁷³, should be negative. However, the basic assumption involved was that the crystal field model was applicable. Crystal field theory is solely electrostatic in nature and does not provide any avenue for the introduction of covalent bonding. The σ -bonding between the metal and the oxo group is predominantly by means of the molecular orbital which has the d_{z^2} metal orbital as an important component. Similarly a molecular orbital composed partially of the d_{xz} and d_{yz} metal orbitals is the principle source of pi-bonding between the two groups. Kon and Sharpless³⁵ have previously indicated that there is considerable pi-bonding between the chlorides and the chromium atom in the CrOCl_5^{2-} species including both the axial and equatorial chlorides. Therefore, it is difficult to ascertain what sort of affect should be expected on the d_{z^2} orbital. On this basis it does not appear that the simple crystal field model can be applied without a great deal of uncertainty in the values obtained for Ds and

Dt. Hence, it seems reasonable to assign this band to the $d_{z^2} \leftarrow d_{xy}$ transition.

Another possibility that cannot be ruled out is a higher energy charge transfer band such as the $e_{\pi}^* \leftarrow e_{\pi}$ transition. Vanquickenborne and McGlynn⁸⁰ predicted this transition to be polarized along the z axis. Hence, one might also expect to observe a vibrational splitting of this band due to the Cr-O vibrational stretching frequency. Therefore, it is not possible to rule out the $e_{\pi}^* \leftarrow e_{\pi}$ transition as the one occurring in the range 25-30kK.

(C) Hydroxy Acid Complexes of Cr(V)

Prior to this work there were no compounds isolated that contained the CrO^{3+} species other than the chloro and fluoro complexes. The elemental analyses of the new compounds prepared here correspond to the empirical formula $Cs_2CrO(AB)Cl_3$, where AB represents the hydroxy acid. The hydroxy acids that yielded isolable complexes are tartaric acid, hydroxy malonic acid, and malic acid. There may be some question as to whether these compounds are actually Cr(V) species (d^1 system) or Cr(IV) species (d^2 system) because of the high magnetic susceptibilities of these complexes (see Table VII). The values for the magnetic moments are in the range expected of a d^2 system, as calculated from the spin-only formula. If one were to include the orbital contribution in a d^1 system the calculated value would rise to 3.00 B.M. However, since the d orbitals in this type of complex are most certainly not degenerate the orbital contribution to the magnetic moment should be

⁸⁰ Vanquickenborne, L.G., and McGlynn, S.P., Theor. chim. Acta, 9, 390 (1968).

reduced considerably if not completely quenched.

Other than the magnetic susceptibility values, all other physical-chemical evidence points to a Cr(V) species (d^1 system). This evidence includes the following data: (1) For a complex of the formula $\text{Cs}_2\text{CrO}(\text{AB})\text{Cl}_3$ the hydroxy acid has to lose two protons rather than just one as it would for a Cr(IV) species and this is what would be expected for a dicarboxylic acid such as tartaric acid, hydroxy malonic acid, or malic acid. (2) If a Cr(IV) species is formed presumably the hydroxy acid would have to react as a reducing agent since the starting material is a Cr(V) complex and it seems unlikely that it would reduce the chromium only to a plus four state rather than the much more stable Cr(III) species. (3) The complexes give a very good ESR signal (see Figure 16). According to Cotton and Wilkinson⁸¹ there has been only slight success at observing ESR resonance under any experimental conditions for paramagnetic ions having an even number of electrons. Of course there remains the possibility that the product obtained, for example from the reaction with tartaric acid, could be contaminated with some $\text{Cs}_2\text{CrOCl}_5$ which was used as a starting material. However, if one compares the ESR spectrum of $\text{Cs}_2\text{CrOCl}_5$ with that of $\text{Cs}_2\text{CrO}(\text{tart})\text{Cl}_3$ the ESR signal is found to be much broader for $\text{Cs}_2\text{Cr}(\text{tart})\text{Cl}_3$ and likewise the $\langle g \rangle$ values are significantly different ($\langle g \rangle = 1.988$ for $\text{Cs}_2\text{CrOCl}_5$ and $\langle g \rangle = 1.969$ for $\text{Cs}_2\text{CrO}(\text{tart})\text{Cl}_3$). Therefore, this seems to rule out

⁸¹Cotton, F.A., and Wilkinson, G., "Advanced Inorganic Chemistry", Interscience Publishers, New York, 1966.

the Cr(IV) plus contamination argument. (4) The Cr-O band in the infrared spectra of these complexes has shifted very little if any from its position in the Cr(V) complex, $\text{Cs}_2\text{CrOCl}_5$. Although this band is not particularly sensitive to changes in the type of ligand coordinated to the metal, it seems reasonable to assume there should be some observable change in the position of this band if there were a change in oxidation state of the metal. (5) Finally, the visible-ultraviolet spectra of these complexes are all similar and seem to fit nicely into the pattern of assignments made for the fluoro and chloro complexes.

An attempt to establish the oxidation state of the chromium by wet chemical analysis was not successful. A known amount of complex was dissolved in a standardized solution of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ with the excess Fe^{2+} (that was not required for reduction of the complex) being determined by titration with a standard solution of $\text{K}_2\text{Cr}_2\text{O}_7$, using diphenylamine sodium sulfonate as an indicator. However, the hydroxy acid present in the complex reduces some of the $\text{Cr}_2\text{O}_7^{2-}$ also, and the amount that it reduces seems to be a function of the concentration of the Fe^{2+} . Therefore no reliable conclusions could be drawn from this method for determining the oxidation state of the metal. Since all of the evidence accumulated other than the magnetic moment data points to a Cr(V) species, it will be assumed that these are indeed Cr(V) complexes of the formula, $\text{Cs}_2\text{CrO}(\text{AB})\text{Cl}_3$.

1. Infrared Spectra

The infrared spectrum of each of the hydroxy acid complexes

has a strong band in the range $935\text{--}950\text{ cm}^{-1}$. This is the region, as was mentioned previously, where one expects to find the Cr-O stretching mode for an oxochromium(V) species. Hence, since the band is not a ligand band it seems reasonable to assume that this band is in fact the Cr-O stretching vibration. Assuming that the axial position is occupied by a chloride ion one would not expect the Cr-O stretching frequency to change very much in going from $\text{Cs}_2\text{CrOCl}_5$ to $\text{Cs}_2\text{CrO}(\text{tart})\text{Cl}_3$ complex.

Each of the hydroxy acid complexes has a strong band in the region $330\text{--}345\text{ cm}^{-1}$ which is the only strong band observed in the $300\text{--}600\text{ cm}^{-1}$ range. Therefore one can feel rather confident in assigning this band to a Cr-Cl stretching vibration. This data is summarized in Table XIV.

TABLE XIV
STRETCHING FREQUENCIES ASSIGNED FOR THE HYDROXY ACID COMPLEXES
OF OXOCHROMIUM(V) (cm^{-1})

Compound	Cr-O	Cr-Cl
$\text{Cs}_2\text{CrO}(\text{tart})\text{Cl}_3$	945 ^a	345
$\text{Cs}_2\text{CrO}(\text{C}_3\text{H}_2\text{O}_5)\text{Cl}_3$	950	330
$\text{Cs}_2\text{CrO}(\text{C}_4\text{H}_4\text{O}_6)\text{Cl}_3$	935	335

^aBands obtained from Nujol mulls using CsI optics.

A number of low intensity bands are observed in each of the

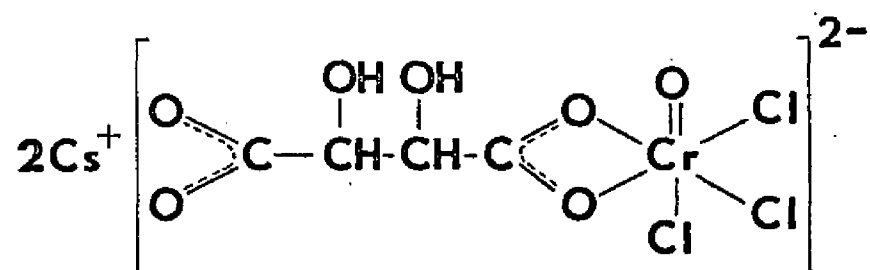
new complexes in the range $430\text{--}630\text{ cm}^{-1}$. As explained by Nakamota⁶⁵ there are two types of bands that one can observe in this region for this type of complex. The first is a Cr-O(chelate) stretching vibration and the second is a ring deformation vibration which usually appears at a slightly higher frequency but with approximately the same intensity as the Cr-O(chelate) stretching vibration. Since the bands observed in this region in the hydroxy acid complexes are all extremely weak no attempt will be made to make definite assignments of these bands. It will have to suffice to say that these weak bands are caused by the Cr-O(chelate) stretching vibration and the ring deformation frequency.

One other point of interest in the infrared spectra of each of the hydroxy acid complexes is that two bands are observed in the carbonyl stretching region. In each case one band is located at the same position as in the non-coordinated hydroxy acid itself. The second occurs at a slightly higher frequency in each case (in the range of $1590\text{--}1635\text{ cm}^{-1}$). Apparently the second carbonyl band is due to the coordination of the carbonyl (through the oxygen) to the chromium.

Although there is no direct evidence as to how the hydroxy acid is coordinated to the metal, it is nevertheless interesting to speculate on this point. Assuming that the hydroxy acid has a negative two charge when coordinated (which it must have if the chromium is in a plus five oxidation state and the molecular formula corresponds to $\text{Cs}_2\text{CrO}(\text{tart})\text{Cl}_3$) there are several ways for coordination to take place. If the hydroxy acid has a negative two charge when coordinating,

it is logical to assume that it is acting as a bidentate ligand. The first possibility is coordination through the two carboxyl groups since they should lose their protons much more easily than the hydroxyl group; but in all three cases two different carboxyl group stretching frequencies are observed indicating that one is coordinated to the metal while the other is not. Furthermore, the tartaric acid and malic acid complexes would have to form a seven-membered chelate ring which does not seem to be very likely.

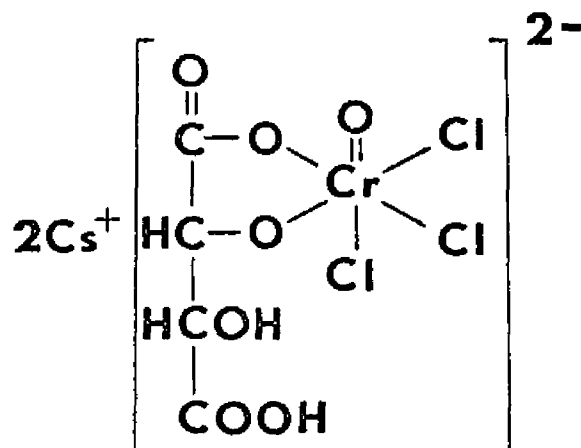
A second possibility is that indicated below:



Note that the hydroxy acid has a negative two charge since both carboxyl groups have lost their protons. This structure should give two different carbonyl group stretching frequencies since one is coordinated and the other is not (but is simply "ionic"). Also, both hydroxyl groups remain relatively unchanged so that there should only be one C-OH frequency and this is what is observed in each of the three complexes. The undesirable feature of this structure is that a four-membered ring must form in coordination. However, this type of structure is known to form with the acetate ion in such compounds as $\text{Cr}(\text{Ac})_3$, $\text{Mn}(\text{Ac})_3$ and $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ ⁸².

⁸²Talbot, J.H., Acta Cryst., 6, 720 (1953).

A third possibility is coordination through one carbonyl group and the hydroxyl group on the adjacent carbon as indicated in structure below:



This structure should give rise to two different carbonyl frequencies and likewise a five-membered ring forms upon coordination, a much more likely situation. However, some changes should be evident in the OH in-plane bending mode (this occurs at 1450 cm^{-1} in both tartaric acid and in the tartrate complex) and also in the C-OH secondary alcohol bending mode which occurs at 1097 cm^{-1} in tartaric acid and at exactly the same place in the tartrate complex.

Therefore, to be consistent with the infrared data the second structure proposed above is more desirable even though a four-membered ring is formed upon coordination.

2. Visible-UV Spectra

As mentioned previously, in a d^1 system four d-d transitions are possible with two of them usually being degenerate particularly in C_{4v} symmetry. In the hydroxy acid complexes the symmetry should be considerably lower than C_{4v} so the degeneracy of the d_{xz} and d_{yz}

orbitals is removed. The first low intensity band which is observed in the spectra falls in the range 10.5-12.5kK and it is split into two or three components. This is very similar to what is found for the chloro complexes and the splitting observed falls in the range 750-950 cm^{-1} . Therefore, it seems likely that this splitting is also vibrational in origin, and to be attributed to the vibronic coupling involving the strong axial Cr-O bond.

The second low intensity band which is observed as a shoulder (possibly two shoulders separated by 800-1000 cm^{-1}) is located in the range 14-15.5kK. The possibility exists that the two shoulders observed could be due to vibrational splitting in a d-d electronic band. Unfortunately, solution spectra of these complexes could not be obtained because of insolubility and decomposition problems. Thus, they are insoluble in inert solvents such as CCl_4 and benzene, and although they do dissolve in DMF and DMSO, decomposition takes place in these solvents as was evident from the visible-ultraviolet spectra.

Because of the frequency, intensity, broadness, and vibrational splitting that is observed for the first two bands, a reasonable suggestion is that these bands correspond to the $d_{xz} \leftarrow d_{xy}$ and $d_{yz} \leftarrow d_{xy}$ transitions. Support for this assignment may be deduced from a paper published by Pence and Selbin⁸³. In this paper the electronic spectral data is reported for a series of low symmetry

⁸³Pence, H.E., and Selbin, J., Inorg. Chem., 8, 353 (1969).

oxomolybdenum(V) complexes of β -diketones with the general formula, $\text{Et}_4\text{NMoOCl}_3(\beta\text{-diketonate})$. This data along with the corresponding band assignments are given in Table XV. As they indicated in their

TABLE XV
VISIBLE-UV SPECTRAL DATA FOR THE MoOCl_3L^-
ANIONS IN ACETONITRILE

L = DBM	L = BTFA	L = TTFA	L = HFA	Assignments
			12.9	
13.6(30)	13.8(32)	13.7(350)	14.2(30)	$d_{xz}, d_{yz} \leftarrow d_{xy}$
18.4(5)	19.2(300)	18.9(300)	18.9(80)	$d_{x^2-y^2} \leftarrow d_{xy}$
19.7(50)	20.5(200)	20.1(400)	20.3(80)	
22.2(420)	[24.1]	[23.8]	[23.7]	
23.7(410)	25.1(4000)	24.9(20,000)	25.4(2600)	$d_{xy} \leftarrow \pi$
	[26.1]			

^aAll frequencies are in kK units

^bExtinction coefficients are in parentheses; shoulder bands are enclosed in brackets.

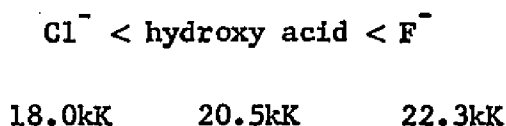
paper, the symmetry of the complexes is so low that the degeneracy of the d levels is expected to be completely removed. The first band which has a shoulder when observed in a Nujol mull at 77°A is assigned the $(d_{xz}, d_{yz}) \leftarrow d_{xy}$ transition. The observed shoulder was thought to be due to vibrational splitting. However, in the region 18-21kK units there are two bands which were assigned to the

$d_{x^2-y^2} \leftarrow d_{xy}$ transition. The first of these two bands appears as a shoulder⁴⁸ in all cases except one with the splitting between the two bands ranging from 1.2-1.6kK. Ordinarily the only type of vibrational splitting observed is thought to be that due to the strong M-O stretching frequency. This splitting does not appear to be vibrational splitting due to the Mo-O because the separation is much larger than what is usually observed for this type of splitting and likewise the polarization of the orbitals involved is not along the Mo-O bond axis. Therefore this observed splitting does not seem to have a vibrational origin. The first shoulder that occurs from 18.4-19.2kK might possibly be the $d_{yz} \leftarrow d_{xy}$ electronic transition. These compounds are certainly low enough in symmetry so that the degeneracy of the d_{xz} and d_{yz} orbitals is removed. As one can see from Table XV there would then be a difference of approximately 5kK in the energies of the d_{xz} and d_{yz} orbitals. At first glance this seems rather large but the band from 18.4-19.2kK occurs as a shoulder and it is difficult to tell exactly where the maximum lies. The fact is that it may actually lie closer to the band observed at 14kK than the assigned value indicates (see reference 84). Likewise one would expect the separation of the d_{xz} and d_{yz} orbitals to be less in a Cr(V) complex than in a Mo(V) complex, assuming the symmetry is approximately the same. If the assignments are correct in the Cr(V) hydroxy acid complexes

⁸⁴Arndts, R.T., Ph.D. Dissertation, Louisiana State University, Baton Rouge, Louisiana, 1969.

the energy separation of the d_{xz} and d_{yz} orbitals is about 3kK units. Therefore one would expect this separation to be greater than 3kK units in the Mo(V) complexes.

The third band that occurs in each of the complexes is located in the range 20.20-21.05kK. The most reasonable assignment of this band is to the $d_{x^2-y^2} \leftarrow d_{xy}$ transition. This seems to fit into the assignments for the chloro and fluoro complexes, since this gives the following (spectrochemical) series based upon the 10Dq values:



Since this transition is crystal field sensitive it should occur at a higher frequency than in the corresponding chloro complex. This holds true also for the tartrate and chloro complexes of VO^{2+} (references 70 and 85) and also for the chloro and oxalate complexes⁸⁶ of MoO^{3+} , although the oxalate complex of MoO^{3+} is a dimer. However the tartrate complex of VO^{2+} (also a dimer) has a higher 10Dq value (16.5kK) than does the fluoro complex of VO^{2+} (15.4kK). The 10Dq value is about 25% larger for the tartrate complex of CrO^{3+} than for the tartrate complex of VO^{2+} but the two complexes are not quite comparable because the chromium is

⁸⁵Selbin, J., and Morpurgo, L., J. Inorg. Nucl. Chem., 27, 673 (1964).

⁸⁶Mitchell, P.C.H., J. Inorg. Nucl. Chem., 26, 1967 (1964).

surrounded also by three chlorides while the vanadium is surrounded by one additional tartrate plus a water molecule. This surely would account for the reversal of the order of 10Dq values for the fluoro and tartrate complexes of VO^{2+} and CrO^{3+} .

The fourth band that occurs in the electronic spectra of each of the hydroxy acid complexes is observed in the range 22.85-23.00kK. A band was observed in the chloro-complexes in just about the same position (22.5kK) and was previously assigned to the $d_{xy} \leftarrow \pi_{\text{Cl}}$ transition. Therefore, it seems logical to assume that this band observed in the spectra of the hydroxy acid complexes is very likely due to the same transition. The arguments presented by Horner and Tyree⁷⁶ would mitigate against the assignment of this band as a charge transfer involving a transition from the oxo group to the d_{xy} orbital of the chromium. Likewise it would not be expected that a transition from the pi orbitals of the ligand to the metal would occur at the same energy as that for the first charge transfer band in the chloro complexes. The former transitions probably lie at a higher energy than those involving the chloro pi orbitals. In going from the chloro to the hydroxy acid complex one might expect little difference in the energy separation of the chlorine pi orbitals relative to the d_{xy} metal orbital. Since the hydroxy acid ligand has a slightly stronger ligand field this might cause the d_{xy} orbital to be raised in energy by a small amount although it does not point directly at the ligand. Therefore, the slightly higher energy involved in this transition involving the hydroxy acid complexes over that of the chloro complex

would be expected.

The last band observed in this series of complexes lies in the range 29.05-29.30kK. This also is analogous to the band observed in the chloro complexes (25-30kK) and in the fluoro complex (27.30-31.50kK). However, in both the chloro and fluoro complexes this band is split into several components which is explained as vibrational splitting. This band is assigned the $d_{z^2} \leftarrow d_{xy}$ transition but the $e_{\pi}^* \leftarrow e_{\pi}$ transition may not be completely ruled out. Hence, it seems likely that this last band observed in the hydroxy acid complexes may also be the $d_{z^2} \leftarrow d_{xy}$ transition. One would expect the position of the d_{z^2} band to shift very little regardless of the type of ligand occupying the axial position since the strongly covalent Cr-O bond is the primary factor in determining the position of the d_{z^2} orbital energy. Assuming that the hydroxy acid is acting as a bidentate ligand there are two different positions about the chromium which the molecule could occupy. Both oxygens from the ligand could be in the cis positions of the equatorial plane or one oxygen could be in the equatorial plane while the second could be in the axial position. If the second structure describes the position of the hydroxy acid one might predict that the d_{z^2} orbital of the metal in the hydroxy acid complex would be slightly higher in energy than in the chloro complex and slightly lower in energy than in the fluoro complex so that the energy of the transition lies in the same order as the $10Dq$ values. If Figures 8, 9, and 10 are examined, this is the way the position of this band lies in the chloro, hydroxy acid, and fluoro complexes of CrO^{3+} . Vibrational splitting does not occur in the hydroxy acid complexes. However, there does

not seem to be any known explanation why vibrational splitting is observed in certain compounds and not in others of seemingly analogous structure and bonding.

SUGGESTIONS FOR FUTURE WORK

There are a number of areas in this study that might serve as a basis for further work. One of the first problems is certainly the preparation of other Cr(V) complexes. A number of avenues have been investigated in this study but there are probably numerous other possibilities for trying to prepare a greater variety of Cr(V) complexes. Possibly it may be just a matter of getting together the correct solvent, starting material, concentration and temperature to provide a method of preparation. With a greater variety of complexes, electronic band assignments could be made with a much greater certainty and a more direct comparison could be made with similar complexes of VO^{2+} and MoO^{3+} .

Another area that needs further investigation is the fluoro complex of Cr(V). Other than what was done in this study no electronic or infrared spectral investigations have been done although KCrOF_4 and AgCrOF_4 have been previously prepared and isolated. Spectral studies of this species could further substantiate the affect on the first d-d transition of an unoccupied axial position. Also, the fluoro complex may serve as a starting material for the preparation of still other Cr(V) complexes.

There are probably other hydroxy acids and indeed other types of ligands similar to hydroxy acids that may work equally as well as the ones that were successfully used for preparation here of new Cr(V) complexes. Likewise with a more carefully planned method it might be possible to resolve, more definitely, the oxidation state

of the chromium by a wet chemical method in the hydroxy acid complexes.

VITA

Orville Vernon Ziebarth was born on August 29, 1936 at Princeton, Minnesota. He received his elementary and secondary school education in the Princeton Public School system. After graduating from high school he attended St. Cloud State College, St. Cloud, Minnesota from which he received his Bachelor of Science degree in 1958.

At this time he married Renee A. Lofquist and since that time has had three sons, Robin Paul, Michael Scott and Thomas Mathew.

After one year of high school teaching at Truman, Minnesota work for the degree of Master of Science was begun. This work was completed in 1962 at Iowa State University, Ames, Iowa, at which time the degree was awarded.

In 1963 he joined the faculty at Kearney State College, Kearney, Nebraska for one semester as an Instructor in the Department of Chemistry.

In the Fall of 1963, he joined the faculty at Mankato State College, Mankato, Minnesota, as an Assistant Professor and taught chemistry at that institution for four years. During the summers of 1964-1967 he attended Louisiana State University as a National Science Foundation participant in the college chemistry teachers program. In 1968 he received a leave of absence from Mankato State College and commenced full time work at the Louisiana State University where he is currently a candidate for the Ph.D. degree.

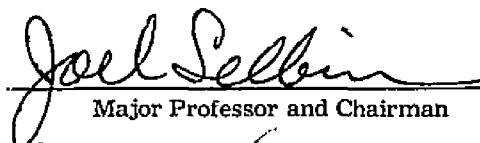
EXAMINATION AND THESIS REPORT

Candidate: Orville V. Ziebarth

Major Field: Chemistry

Title of Thesis: Preparation and Spectral Properties of Oxochromium(V) Complexes

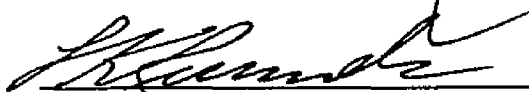
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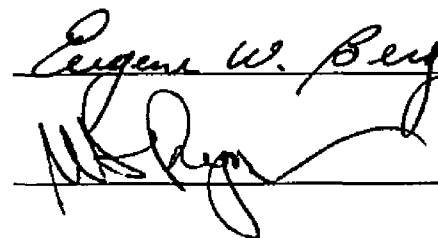

Major Professor and Chairman


Dean of the Graduate School

EXAMINING COMMITTEE:









Date of Examination:

August 4, 1969